Functionalized Iron Hydroxyapatite as Eco-friendly Catalyst for NH$_3$-SCR Reaction: Activity and Role of Iron Speciation on the Surface

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Eco-friendly catalysts have been obtained by functionalizing hydroxyapatite (HAP) with iron (Fe/HAP), according to three preparative methods (flash ionic exchange, deposition-precipitation, and impregnation). Fe/HAP samples (ca. 2–7 wt.% Fe) have been tested in the reaction of NO$_x$ reduction by ammonia (NH$_3$-SCR) in the 120–500 °C interval with different NH$_3$/NO ratios (0.6–2) at fixed contact time (0.12 s). All Fe/HAP samples were active and selective in the NH$_3$-SCR reaction starting from ca. 350 °C. Better performances have been observed on catalysts prepared by deposition-precipitation and impregnation (about 70% of NO$_x$ conversion and selectivity to N$_2$ higher than 95% at 350 °C), where α-Fe$_2$O$_3$ and 3D-Fe$_3$O$_4$ nanoclusters were present, as indicated by Mössbauer and UV-Vis-DR spectroscopies. On the opposite, paramagnetic Fe$^{3+}$ centres were the predominant species on samples prepared by flash ionic exchange. Further characterization techniques (XRPD, N$_2$-physisorption, acidity by NH$_3$ desorption, and H$_2$-TPR) have concurred to elucidate Fe-sitting HAP and structure-activity relationships.

Introduction

Nowadays, catalytic technologies represent the most effective and common solution to environmental issues related to air, water, and soil pollution. Although catalysis can be considered a well consolidated field, the need to meet ever more stringent criteria of sustainability and efficiency requires a continuous effort to improve and optimize the current catalytic processes and related catalytic materials.[1] Actually, the development of high performance, non-toxic, low-cost and eco-friendly materials to be used as catalysts is a key factor for the achievement of a sustainability-driven environmental catalysis.

Selective catalytic reduction by ammonia (NH$_3$-SCR) is the most commonly used process for the abatement of nitrogen oxides (NO$_x$), which are considered major pollutants in air.[2] Some reactions starting from NO or NO$_2$ can occur according to the Equations (1) to (4):

\[
\begin{align*}
4\text{NO} + 4\text{NH}_3 + \text{O}_2 & \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \text{ “standard SCR”} \\
6\text{NO} + 4\text{NH}_3 & \rightarrow 5\text{N}_2 + 6\text{H}_2\text{O} \text{ “slow SCR”} \\
6\text{NO}_2 + 8\text{NH}_3 & \rightarrow 7\text{N}_2 + 12\text{H}_2\text{O} \text{ “NOx SCR”} \\
\text{NO} + \text{NO}_2 + 2\text{NH}_3 & \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O} \text{ “fast SCR”}
\end{align*}
\]

Despite the industrial and commercial success of NH$_3$-SCR process, this process is undergoing a constant evolution aimed to satisfy the stringent standards for NO$_x$ emission.[3]

Several materials have been proposed, studied, and successfully employed as catalysts in the NH$_3$-SCR reaction over the years. In the last decades, the use of metal exchanged zeolites as SCR catalysts has become widespread. However, the expensiveness of zeolite synthesis as well as some practical disadvantages of zeolite-based catalysts (e.g. poor hydrothermal stability, low resistance to sulfur poisoning) constitute no-negligible limitations of these systems and an unequivocal stimulus to develop valid alternatives.

Recent studies[4–7] have demonstrated that the deposition of transition metal species (e.g. Ag, Cu, Fe) onto calcium hydroxyapatite results in effective catalysts for NH$_3$-SCR reaction. Stoichiometric calcium hydroxyapatite (HAP, chemical formula Ca$_{10}$(PO$_4$)$_6$(OH)$_2$) is an inorganic compound that can be found in nature as mineral or main inorganic component of mammal bones. HAP crystal lattice is characterized by a hexagonal symmetry (space group P6$_3$/m) assured by a three-dimensional framework of hexagonally packed tetrahedral PO$_4^{3–}$ ions. Ca$^{2+}$ ions are located in two non-equivalent crystallographic sites, Ca(1) and Ca(2) sites, which are characterized by a different coordination number (9 and 7, respectively) and environment.[8] The high mobility of Ca$^{2+}$ ions and the high coordination number of both Ca sites allow their substitution in both Ca(1) and Ca(2) positions by several cations,
many of them of catalytic interest. In addition, many anions can replace either OH\(^-\) or PO\(_4\)^{3-} ions or both.\[^{[9]}\] This intrinsic capability to exchange the framework ions and allocate other metal species, similarly to zeolites, together with the amphoteric character of HAP surfaces allow obtaining interesting functionalized materials, which are experiencing a growing success in heterogeneous catalysis.\[^{[10–12]}\]

Actually, copper-hydroxyapatites (Cu/HAP) have exhibited remarkable performances in terms of activity, selectivity and durability when tested as catalysts in NH\(_3\)-SCR reaction.\[^{[9,11]}\] The copper precursors as well as the deposition procedure affect the copper speciation onto the hydroxyapatite surfaces and the catalytic performance of Cu/HAP in NH\(_3\)-SCR, as demonstrated by Gervasini et al.\[^{[11]}\] It was found that the Cu/HAP catalysts prepared starting from copper nitrate, as precursor, could be associated with the best active and selective SCR catalysts. In addition, an optimum Cu-concentration on HAP of ca. 6 wt.% was observed independently of the used Cu-deposition method.

A recent comparative study between copper- and iron-modified HAP catalysts prepared by ion exchange procedure\[^{[18]}\] revealed that both catalyst series were active and selective for many of them of catalytic interest. In addition, many anions can replace either OH\(^-\) or PO\(_4\)^{3-} ions or both.\[^{[9]}\] This intrinsic capability to exchange the framework ions and allocate other metal species, similarly to zeolites, together with the amphoteric character of HAP surfaces allow obtaining interesting functionalized materials, which are experiencing a growing success in heterogeneous catalysis.\[^{[10–12]}\]

In this work, calcium hydroxyapatite has been functionalized with iron in different amount (ca. 2–7 wt.%) from iron(III) nitrate, as precursor, according to three preparative methods (flash ionic exchange, deposition-precipitation and wetness impregnation). Depending on the specific experimental conditions, the added iron centres could be allocated as isolated species in two different sites with different coordination environment (Ca(1) and Ca(2)), or alternatively undergo surface agglomeration with formation of Fe-aggregates of different size. A suite of characterization techniques (Mössbauer and UV-Vis spectroscopies, XRPD, \(N_2\)-physisorption, acidity by NH\(_3\) adsorption, and \(H_2\)-TPR) was also used to investigate on iron speciation and sitting on HAP and to deduce relevant structure-activity relationships.

**Experimental section**

**Material used and catalyst preparation**

Hydroxyapatite used (AV15012 lot) was kindly supplied by Solvay, Belgium (Soda Ash & Derivatives Department); its preparation procedure, composition and main properties are detailed in Ref. [14]. As-obtained hydroxyapatite sample was thermally treated at 500 °C for 1 h with controlled temperature rate (1 °C/min) before any successive treatment.

The functionalized hydroxyapatite samples with different iron-loading (in the range 2–7 wt.%) were prepared by depositing Fe(III) nitrate on hydroxyapatite surface with three different procedures: \(i\) a modified ionic exchange procedure, named flash ionic exchange; \(ii\) deposition-precipitation; and \(iii\) incipient wetness impregnation. For each preparation, HAP in powder, previously dried at 120 °C overnight, was used; the detailed procedures of each type of preparation are below reported.

**Flash ionic exchange**

Three samples (with iron loading in the range 2–7 wt.%) were prepared by flash ionic exchange procedure, a modified procedure compared to the conventional one, specially developed to obtain well dispersed and isolated Fe\(^{3+}\) centres on the hydroxyapatite surface, starting from an aqueous solution of a Fe-salt precursor.

For each preparation, 250 mL of iron(III) nitrate (Fe(NO\(_3\))\(_3\)-9H\(_2\)O) solution (concentration range from 0.005 to 0.035 M) were first thermostatated at 40 °C. To avoid the precipitation of iron(III) hydroxide, the pH was adjusted to value of ca. 3 by HNO\(_3\) addition. Weighed amount of HAP powder (typically ca. 6 g) was added to the iron(III) nitrate solution and the suspension was kept under stirring for 15 minutes. This short time guarantees both preserving surface and structural properties of HAP, which is known to be sensitive to amorphization and it can dissolve under acidic condition,\[^{[13]}\] and hindering self-agglomeration of Fe\(^{3+}\) species. The obtained pale yellow samples were filtered, washed with deionized water, and dried at 120 °C overnight, finally calcined at 500 °C for 1 h at controlled rate (1 °C·min\(^{-1}\)) under static air. The collected samples were labelled as Fe\(_x\)/HAP\(_y\), where \(X\) is the nominal Fe loading, in wt.%.\[^{[15]}\]

**Deposition-precipitation**

Two samples (with iron loading of 5 and 7 wt.%) were prepared by deposition-precipitation procedure.

For each preparation, 250 mL of iron(III) nitrate (Fe(NO\(_3\))\(_3\)-9H\(_2\)O) solution (concentration range from 0.0226 M or 0.0324 M) were prepared at room temperature (r.t.); the pH of solution was adjusted to the value of ca. 3 by HNO\(_3\) addition to prevent the precipitation of iron (III) hydroxide. The sample preparation was carried out in a four necked flask, provided with thermometer and reflux condenser; 100 mL of 0.2 M NaOH solution were put in the flask and thermostated at 40 °C under stirring (250 rpm). A given amount of HAP powder (typically ca. 6 g) was introduced to NaOH solution before the addition of the previously prepared solution of iron(III) nitrate by a syringe pump with regular flow rate (1 mL·min\(^{-1}\)). The suspension was maintained under stirring till complete addition of iron-solution, while the pH of the solution was maintained to values of 9–11 by addition of small quantities of NaOH solution (0.2 M). The precipitate was filtered and thoroughly washed with deionized water to remove the excess of sodium hydroxide. The obtained brown sample was dried at 120 °C overnight and calcined at 500 °C for 1 h at controlled rate (1 °C·min\(^{-1}\)) under static air. The collected
Incipient wetness impregnation

Two samples (with iron loading of 5 and 7 wt.%) were prepared by incipient wetness impregnation procedure. For each preparation, 10 mL of Fe(NO\textsubscript{3})\textsubscript{3}-9H\textsubscript{2}O solution (concentration range 0.565 M or 0.809 M) were prepared; the pH of solution was maintained at value of ca. 5 by HNO\textsubscript{3} addition. A weighted amount of HAP powder (typically ca. 6 g) was put in a necked flask and connected to a Büchi rotary evaporator, maintained at 80 °C. The Fe impregnation was performed by adding the iron (III) solution dropwise to HAP, using a dropping funnel connected to the rotary evaporator and alternating cycles of dropping of the Fe-solution and solvent evaporation. The addition of iron solution to HAP lasted a total of 4–5 h. The obtained brown sample was dried at 120°C overnight and calcined at 500°C for 1 h at controlled rate (1°C\cdot min\textsuperscript{-1}) under static air.

The prepared samples were labelled as FeX/HAP\textsubscript{en}, where X is the nominal Fe loading, in wt.%.

Catalyst characterisation

X-ray powder diffraction (XRPD) spectra were collected with a Philips PW 3020 powder diffractometer, fitted with PW 1830 generator and copper tube (CuK\textsubscript{α1}=1.54060 Å) and equipped with X-ray source operating at 40 kV and 25 mA. Powder diffractograms were collected by continuous scan in the 2θ range from 10° to 60°, step size of 0.05° 2θ, time for step of 5 sec, scan speed of 0.010 2θ s\textsuperscript{-1}, number of steps of 1000, and total time of 1 h 23 min.

Specific surface area (S.S.A.), pore volume, and pore size distribution of the samples were determined by adsorption and desorption isotherms of N\textsubscript{2} (99.9995 % purity) at −196°C by using an automatic analyser of surface area (Sorptomatic 1990 version instrument from Thermo Scientific Carlo Erba). The samples (ca. 0.2 g sieved as particles in the range of 80–200 mesh) were outgassed at 350°C for 4 h under vacuum, in order to remove water and other volatile organic compounds adsorbed on the surface. The specific surface area values were computed using 3-parameters BET (Brunauer-Emmett-Teller) equation. The pore volume and pore size distribution were determined with the Software OriginPro8 by using combinations of Gaussian methods.

Mass loss of bare and Fe-loaded hydroxyapatite samples was determined by thermogravimetric analysis (TGA 7, Perkin Elmer analyser). Prior to the analysis, the samples were dried at 120°C overnight and a weighted amount (ca. 10–15 mg) was loaded on the pan of the thermobalance. Each experiment was carried out under air flowing gas (30 mL·min\textsuperscript{-1}) with the following method: i) isothermal step at 35°C for 5 min; ii) heating from 35 to 500°C at 10°C·min\textsuperscript{-1}; iii) isothermal step at 500°C for 60 min; and iv) cooling to 40°C.

Acidity of both bare hydroxyapatite and Fe loaded catalysts was evaluated by NH\textsubscript{3} probe adsorption by flowing dynamic experiments. The sample, previously pressed, crushed, and sieved to obtain particles in the range 45–60 mesh, was dried and weighed (ca. 0.20 g). It was then put on a porous septum in a quartz reactor and maintained at 120°C for 30 min under flowing air; then, it was contacted with a NH\textsubscript{3}/He mixture flow (6 NL·h\textsuperscript{-1}) at NH\textsubscript{3} concentration of ca. 500 ppm. The NH\textsubscript{3} concentration vented by the reactor was continuously monitored by an online FT-IR spectrophotometer (Bio-Rad, DTGS detector equipped with a multiple reflection gas cell, path length 2.4 m) at 966 cm\textsuperscript{-1}. On each sample, NH\textsubscript{3} was completely adsorbed for a given measured time, as observed from the trace of the NH\textsubscript{3} line at 966 cm\textsuperscript{-1}, that was recorded as a function of time. When the saturation of the acid sites under the flowing NH\textsubscript{3} concentration was attained, the NH\textsubscript{3} signal restored at level corresponding to its concentration in the starting mixture. From the evaluation of the time during which the NH\textsubscript{3} signal remained to zero, the amount of acid sites has been evaluated, as reported in Equation (5):

\[
\frac{\text{pmoles of NH}_3(\text{ads})}{\text{mg of sample}} = \frac{\text{NH}_3(\text{fed})}{\text{RT} \cdot \text{m}_{\text{sample}}} \cdot \frac{F \cdot t \cdot P}{\text{C}_{\text{NH}_3}},
\]

where \(\text{NH}_3(\text{fed})\) is the flowing NH\textsubscript{3} concentration (ppm); \(F\) is the total flow rate of NH\textsubscript{3}/He mixture (in NL·h\textsuperscript{-1}); \(t\) is the time during which NH\textsubscript{3} was completely adsorbed (in min); \(P\) is the pressure (in atm) and \(m_{\text{sample}}\) is the mass of the sample (in g).

Assuming a 1:1 stoichiometry for the NH\textsubscript{3} adsorption on the surface acid site, the amount of acid sites per sample mass or per surface unit (in μequiv·g\textsuperscript{-1} or μequiv·m\textsuperscript{-2}) was evaluated. Measurements were replicated and in all cases a percent relative uncertainty of less than 3 % was obtained.

Reduction analyses in programmed temperature (H\textsubscript{2}-TPR) were realized on fresh Fe/HAP samples. A TPDRO–1100 (from Thermo Scientific) equipped with a thermal conductivity detector (TCD), a quartz reactor, and a filter filled with soda lime for trapping acid gas were used. The TPR measurement was carried out using H\textsubscript{2}/Ar (5.00% v/v) as reducing gas mixture. The gas flow rate was adjusted by mass flow controllers to 20 cm\textsuperscript{3}·min\textsuperscript{-1}. The obtained TPR peaks were integrated for quantitative determination of H\textsubscript{2} consumed; calibrations were performed with CuO bulk as reference material. TPR runs were carried out by heating a step from r.t. to 900°C, at rate of 10°C·min\textsuperscript{-1}. Dried sample mass in powder (ca. 0.07–0.2 g, equivalent to about 35–45 μmol of Fe\textsubscript{3}O\textsubscript{4}) was used, this allowed to maintain the values of the sensitivity and resolution parameters\textsuperscript{[16-17]} around 120 s and 20°C, respectively, for all the analyses.

The experimental H\textsubscript{2}-TPR curves obtained have been decomposed with the Software OriginPro8 by using combinations of Gaussian functions.

Spectroscopic characterisation

Mössbauer spectra were obtained in transmission geometry with a 512-channel constant acceleration spectrometer (WissEl, Germany), using a source of 57Co in Rh matrix of nominally 50 mCi. The sample ideal thickness was evaluated considering the weight percentages of the different elements of each catalyst (about 100 mg of powder were used for a holder of 1.8 cm of diameter). Velocity calibration was performed using a 12-μm-thick α-Fe foil as reference. Spectra were collected at −260 and 25°C. Measurements at low temper-
Catalytic performances of iron loaded catalysts in NH\textsubscript{3}-SCR reaction were evaluated by using a continuous laboratory-reaction line equipped with a set of mass flow controllers (Bronkhorst, Hi-Tec and Brooks Instruments), a tubular vertical electric oven (Eurotherm Controller-Programmer type 818), a glass tubular catalytic micro reactor (5 mm i.d.), and an on line FT-IR spectrophotometer (Bio-Rad, DTGS detector) for qualitative and quantitative determination of the fed and vented gaseous species. For each experiment, the catalyst samples (about 0.20 g), previously pressed, crushed and sieved so as to obtain particles in the range 45–60 mesh, were dried at 120 °C overnight. Then, they were pre-treated in situ under O\textsubscript{2}/N\textsubscript{2} flow (20% v/v) at 120 °C for 30 min. The catalyst activity was studied as a function of the temperature (120–200 °C), maintaining constant the concentration of feeding gas mixture and with a total flow rate of 6 NL·h\textsuperscript{-1} (corresponding to contact time of 0.12 s). Each temperature was maintained for 60 min in order to allow the attainment of the steady-state condition. The temperature was increased at step ramping the temperature at 10 °C·min\textsuperscript{-1}. The fed mixture was prepared mixing about 500 ppm of NO, 500 ppm of N\textsubscript{2}O, and about 10,000 ppm of O\textsubscript{2} in nitrogen. After the mixing, the effective fed mixture contained also NO\textsubscript{2} (about 50 ppm of NO\textsubscript{2}). The gas-mixture flowed through the catalyst particles at 120 °C until the catalyst surface was saturated with NH\textsubscript{3}.

Additional NH\textsubscript{3}-SCR catalytic tests were also performed by varying the fed NH\textsubscript{3} concentration (from 300 to 1000 ppm) at fixed NO concentration (500 ppm) in the same temperature range and contact time (0.12 s).

The gaseous stream vented from the reactor was monitored by a FT-IR equipped with a multiple reflection gas cell (with 2.4 m path length; resolution of 2 cm\textsuperscript{-1}; sensibility of 1.5 and 92 scans per 180 seconds) for quantifying the unconverted reagents and/or reaction products. The total absorbance of all the IR active species (Gram–Schmidt profile) flowing from the reactor was continuously recorded as a function of time, while the reaction temperature was changing.

The NO, NO\textsubscript{2}, and N\textsubscript{2}O and other formed species (if any) were quantified from the peak height of a selected absorbance line, considering the measured calibration factors. N\textsubscript{2}O concentration was determined from the difference between the fed NH\textsubscript{3} and NO, (NO plus NO\textsubscript{2}) concentrations and the sum of the unreacted NH\textsubscript{3} plus NO + N\textsubscript{2}O + NO\textsubscript{2} concentrations, eventually formed. Computational details can be found in Supplementary Material (Table S1).

### Results and Discussion

#### Fe/HAP samples and properties

Bare calcium hydroxyapatite, used as support for Fe/HAP catalysts, was characterized after calcination at 500 °C in order to remove water and any other impurities and to stabilize its structure. Thermally treated HAP is a mesoporous solid with a specific surface area of 53 m\textsuperscript{2}·g\textsuperscript{-1} and a pore size distribution centred at ca. 8 nm (Table 1). The experimental diffractogram of calcined HAP obtained from XRPD analysis contained all the characteristic features of the HAP reference pattern from ICDD PDF database (JCPDS 00-009-0432), thus confirming the crystallinity of the material.

Hydroxyapatite has been functionalized with different amount of iron (from 2 to 7 wt.%) introduced with three

### Table 1. Main morphological and surface properties of Fe/HAP samples

| Code | Fe Loading\textsuperscript{[a]} | S.S.A.\textsuperscript{[b]} \[m\textsuperscript{2}·g\textsuperscript{-1}\] | N\textsuperscript{[c]} \[\%\] | Pore Volume\textsuperscript{[d]} \[cm\textsuperscript{3}·g\textsuperscript{-1}\] | Mean Pore Radius\textsuperscript{[e]} \[nm\] | Acidity\textsuperscript{[f]} \[µmol\textsubscript{H}⁺/g\textsubscript{HAP}\] |
|------|-------------------------------|---------------------------------|---------|----------------|----------------|----------------|
| HAP/500\textsuperscript{[x]} | - | 53 | 2 | 0.19 | 8.2 | 126.6 ± 7 |
| Fe2/HAP\textsubscript{[x]} | 2.07 | 68 | 5 | 0.21 | 6.8 | 198.1 |
| Fe5/HAP\textsubscript{[x]} | 4.77 | 69 | 4 | 0.20 | 6.4 | 204.9 ± 2 |
| Fe7/HAP\textsubscript{[x]} | 6.83 | 76 | 85 | 0.24 | 6.4 | 218.0 |
| Fe5/HAP\textsubscript{[y]} | 4.26 | 84 | 11 | 0.24 | 6.7 | 145.2 ± 4 |
| Fe7/HAP\textsubscript{[y]} | 6.32 | 76 | 2 | 0.20 | 7.3 | 149.0 |
| Fe5/HAP\textsubscript{[z]} | 5.00 | 71 | 4 | 0.21 | 7.0 | 147.4 ± 9 |
| Fe7/HAP\textsubscript{[z]} | 7.00 | 64 | 4 | 0.19 | 6.6 | 151.3 ± 1 |

\[\textsuperscript{[a]}\] Bare HAP calcined at 500 °C for 1 h, \[\textsuperscript{[b]}\] Obtained by atomic absorption, \[\textsuperscript{[c]}\] Specific Surface Area determined by 3-parameters BET equation, \[\textsuperscript{[d]}\] Computed average number of adsorbed N\textsubscript{2} layers, \[\textsuperscript{[e]}\] at p/p\textsubscript{0} = 0.95, \[\textsuperscript{[f]}\] Determined by BJH model from desorption branch of the isotherm (0.3 < p/p\textsubscript{0} < 0.95). For repeated acidity tests, standard deviation is reported.
different methods: flash ionic exchange, deposition-precipitation, and wetness impregnation.

In the first method, the well-known Ca\(^{2+}\) exchange ability of HAP has been exploited for preparing three samples containing different concentration of dispersed Fe\(^{3+}\) species with homogenous distribution at the HAP surface. The Fe-concentration of the three Fe/HAP catalysts, as determined by ICP analysis on the digested samples, are reported in Table 1. The lower or higher amount of iron of the samples did not cause any structural modification. XRP-diffractions of bare HAP and Fe/ HAP\(_e\) are shown in Figure 1a and 1d. Only the pattern of typical crystalline HAP (JPDF 00-09-0432) can be individuated without presence of lines typical of the most stable iron oxide/hydroxide phases. The introduction of iron species by flash ion exchange influenced the morphological properties of the samples, i.e., surface area, pore volume and pore size distribution (Table 1). As a general trend, a slight increase in the specific surface area and pore volume values was observed after iron functionalization of HAP, whereas mean pore radius decreased. Moreover, the higher the loading, the more significant were the differences compared to bare HAP.

Although a different aggregation state of the iron species was expected when deposition-precipitation (DP) and wetness impregnation (WI) procedures were employed to functionalize HAP surface, XRPD analysis allowed to rule out the growth of Fe-aggregates and/or crystalline iron phase in these samples. Indeed the hydroxyapatite was the unique detectable crystalline phase in all the obtained diffractograms of the Fe-samples prepared by DP and WI (Figure 1, b and c). On the other hand, more pronounced variations in the morphological features among the samples could be observed. Similarly to Fe/HAP\(_e\) catalyst series, an increase in the specific surface area values associated with an increase in pore volume and a decrease of mean pore radius were detected also in this case.

To assess the complete removal of residual precursors, thermogravimetric analysis (TGA) was carried out on both the dried and calcined Fe/HAP samples. The TGA analyses (Figure S2) in the temperature range from 35 to 500 °C revealed only water desorption in an amount lower than 5 wt.% for the dried and lower than 2.5 wt.% for the calcined samples prepared by flash ionic exchange and deposition-precipitation. Conversely, the TGA analyses of the dried Fe/HAP\(_w\) samples (Figure S2, f and g) revealed also the additional presence of other mass loss events, likely due to nitrate species decomposition. Anyway, TGA results on the calcined samples confirmed the complete removal of nitrates after calcination.

The Fe/HAP samples are expected to possess well developed acidic sites thanks to the dispersed iron phase on hydroxyapatite surface, which is an amphoteric surface with both basic and acid sites.\(^{[16]}\) Acidity measurements have been performed by adsorption of ammonia, chosen as basic probe for its high basicity (Proton Affinity 8.53 kJ·mol\(^{-1}\)) and because it is a reagent of our studied reaction. Table 1 reports the results obtained in terms of total amount of adsorbed ammonia. As expected, the acidity of HAP increases by iron addition, independently of the used method of iron deposition. In particular, a well increasing trend of acidity with the iron concentration has been observed for the samples prepared by ion exchange method (HAP/500 < Fe2/HAP\(_e\) < Fe5/HAP\(_e\) < Fe7/ HAP\(_e\)). Results do not follow the same trend of the iron amount in the samples, with no regular increase of acidity with iron concentration (Table 1). The first iron addition on HAP (Fe2/ HAP\(_e\)) led to a very high increase of the acid sites, while a lower increase of acidity was observed for the successive Fe-additions (Fe5/HAP\(_e\) and Fe7/HAP\(_e\)). Likely, the first amount of added Fe\(^{3+}\) could be accommodated on the HAP surface and/or in the exchange Ca(I) or/and Ca(II) positions of HAP, then, some degree of aggregation of the Fe phase could occur for further Fe-addition. For the samples prepared by deposition-precipitation and wetness impregnation methods, a more limited acidity has been determined (HAP/500 < Fe5/HAP\(_{w}\) < Fe7/HAP\(_{w}\) and HAP/500 < Fe5/HAP\(_{w}\) < Fe7/HAP\(_{w}\)). For these samples, it can be guessed some more aggregation of the iron centres on the HAP surface than on the samples prepared by ion exchange.
**NH$_3$-SCR catalytic results**

The intrinsic amphotericity of HAP support together with the redox activity of iron centres makes Fe/HAP samples promising candidates as NH$_3$-SCR catalysts, as already presented in a recent paper.$^{[13]}$ HAP possesses both acid sites (attributed to Ca$^{2+}$, surface HPO$_4^{2-}$, and OH$^-$ vacancies) and basic sites (associated with PO$_4^{3-}$ and OH$^-$) which can interact with NH$_3$ and NO, respectively, thus contributing to increase their surface concentration, which could give positive consequence on catalytic activity.

It is also known that the procedure for metal addition on hydroxyapatite surface can affect the catalytic behaviour of the obtained samples, as reported for Cu/HAP.$^{[11]}$ Herein, the catalytic performances of Fe/HAP samples prepared by the three different procedures have been evaluated in the NH$_3$-SCR reaction in the 120–500 °C interval, working at fixed contact time (0.12 s) and starting, at first, from an equimolar NH$_3$/NO mixture.

Profiles of conversion of the fed species (NO$_x$ and NH$_3$) and selectivity to the main products obtained on all the Fe/HAP samples are reported in Figure 2 and Figure 3 as a function of the reaction temperature. All the catalysts were active in the NH$_3$-SCR reaction. In particular it can be observed that a low Fe-concentration on HAP was sufficient to impart good de-NO$_x$ activity to HAP. Actually, when tested as catalyst, bare HAP gave only ca. 20% of NO$_x$ conversion in the range 300–400 °C (Figure S3) thanks to the above described acidic and basic sites of HAP, while the addition of only 2 wt.% of iron gave a sensitive increase of conversion up to approximatively 55% (Table 2). On the other hand, increasing the Fe-concentration from 2 wt.% up to 7 wt.% did not lead to clear differences in the catalyst conversion/selectivity and in general the optimal iron concentration seems to be ca. 5 wt.% (Table 2).

Concerning the formed products from NO$_x$ conversion, in all the cases N$_2$O was the only observed species besides N$_2$. It has to be remarked that in general a very high selectivity to dinitrogen has been obtained even in the presence of strong oxidizing conditions (10,000 ppm of O$_2$). However, some interesting differences emerged when catalysts prepared by different procedures were compared. For the samples prepared by flash ionic exchange (Figure 2, a–c), the maximum NO$_x$ conversion was attained between 300 and 400 °C (Table 2); above this temperature the unselective NH$_3$ oxidation occurred.

**Figure 2.** NH$_3$-SCR catalytic results on Fe/HAP samples prepared by flash ionic exchange (a–c): profiles of conversion of the fed species (NO$_x$ and NH$_3$) and selectivity of formed species (N$_2$ and N$_2$O) as a function of reaction temperature with the use of NH$_3$/NO ratio equal to one.
with undesired formation of N₂O. Consequently, the selectivity to N₂ was very high (98%, Table 2) up to 400°C, while it gradually decreased down to 85% in the range 400–500°C due to non-negligible formation of N₂O (ca. 15% of selectivity to N₂O at 500°C, Table 2). Differently, the samples prepared either by deposition-precipitation or by wetness impregnation (Fig-

Table 2. Main catalytic results on Fe/HAP in NH₃-SCR reaction.

| Code   | NH₃/NO | \(T_{\text{max.conv.NOx}}\) [°C] | NO\(_x\) Conversion\(^{\text{a}}\) [%] | NH₃ Conversion\(^{\text{c}}\) [%] | N₂ Selectivity\(^{\text{d}}\) [%] | \(10^5\) Specific Activity\(^{\text{e}}\) [mol\(_{\text{N}_2}\)·(mol\(_{\text{Fe}}\)·s)] |
|--------|--------|-------------------------------|---------------------------------|-----------------|-----------------|---------------------------------|
| Fe/HAP | 0.6    | 400                           | 36.9                            | 86.4            | 94.7            | 4.85                            |
| 1      | 400    | 350                           | 49.8                            | 51.9            | 97.6            | 6.32                            |
| 2      | 400    | 400                           | 47.0                            | 34.7            | 93.9            | 6.19                            |
| Fe/HAP | 0.6    | 400                           | 45.7                            | 84.7            | 94.5            | 2.41                            |
| 1      | 400    | 400                           | 65.1                            | 73.2            | 95.4            | 3.54                            |
| 2      | 400    | 400                           | 63.7                            | 38.7            | 91.6            | 3.21                            |
| Fe/HAP | 0.6    | 350                           | 38.5                            | 59.2            | 94.8            | 1.29                            |
| 1      | 400    | 400                           | 56.6                            | 64.1            | 94.1            | 1.86                            |
| 2      | 350    | 400                           | 58.7                            | 61.3            | 94.7            | 1.47                            |
| Fe/HAP | 0.6    | 350                           | 59.9                            | 79.0            | 94.7            | 1.86                            |
| 1      | 350    | 350                           | 51.6                            | 41.5            | 92.9            | 3.31                            |
| 2      | 350    | 350                           | 61.1                            | 81.7            | 95.1            | 2.63                            |
| Fe/HAP | 0.6    | 325                           | 65.6                            | 33.1            | 94.1            | 2.34                            |
| 1      | 325    | 325                           | 66.9                            | 33.1            | 94.1            | 2.34                            |
| 2      | 325    | 325                           | 66.4                            | 31.0            | 96.0            | 2.75                            |
| Fe/HAP | 0.6    | 350                           | 66.9                            | 34.8            | 94.5            | 1.90                            |

\(^{\text{a}}\) Temperature of maximum NO\(_x\) conversion, \(^{\text{b to e}}\) Evaluated at temperature of maximum NO\(_x\) conversion.

Figure 3. NH₃-SCR catalytic results on Fe/HAP samples prepared by deposition-precipitation (a–b) and incipient wetness impregnation (c–d); profiles of conversion of the fed species (NO\(_x\) and NH₃) and selectivity of formed species (N₂ and N₂O) as a function of reaction temperature with the use of NH₃/NO ratio equal to one.
ure 3) reached a maximum NO\textsubscript{x} conversion at lower temperature (ca. 300–350°C, Table 2), compared to the Fe/HAP\textsubscript{e} samples. At higher reaction temperatures (T > 350°C), NH\textsubscript{3} started to be oxidised to N\textsubscript{2}O with a deep drop of NO\textsubscript{x} conversion to N\textsubscript{2}. Hence, a higher selectivity to N\textsubscript{2}O was observed (ca. 25–35% at 500°C, Table 2) to the detriment of N\textsubscript{2} selectivity, which decreased down to 70% at 500°C. Therefore, from the comparison among the three catalyst series, it emerges that Fe/HAP\textsubscript{e} were more able to selectively convert NO\textsubscript{x} to N\textsubscript{2} in a broader temperature window than Fe/HAP\textsubscript{DP} and Fe/HAP\textsubscript{IE}. The peculiar behaviour of Fe/HAP\textsubscript{e} catalysts could be ascribed to the speciation of the iron phase, dispersed Fe\textsuperscript{3+} centres being the principal species on all the Fe/HAP\textsubscript{e} surfaces (see next paragraph).

The effect of feeding NH\textsubscript{3}/NO ratio on NO\textsubscript{x} conversion has also been investigated by exploring the catalytic performances of Fe/HAP catalysts in the presence of an excess or a defect of ammonia (Table 2). As expected, a defect of NH\textsubscript{3} in the fed gases (NH\textsubscript{3}/NO = 0.6) led to a moderate conversion of NO\textsubscript{x} associated with high NH\textsubscript{3} conversion, if evaluated at temperature of maximum NO\textsubscript{x} conversion, independently of Fe-loading, as observed on Fe/HAP\textsubscript{DP} samples. On the opposite, any clear positive effect on NO\textsubscript{x} conversion or N\textsubscript{2} selectivity cannot be observed working with an excess of NH\textsubscript{3} in the fed gases (NH\textsubscript{3}/NO = 2) on all the catalysts. A closer look to the results obtained working with NH\textsubscript{3}/NO = 2 showed that on the highest Fe-concentrated catalysts (Fe\textsubscript{7}/HAP\textsubscript{DP} and Fe\textsubscript{7}/HAP\textsubscript{IE}) an increase of NO\textsubscript{x} conversion occurred (Figure 4, d and f; and Table 2). Also in this case, an effect of iron speciation could be guessed to justify this behaviour (see next paragraph).

An insight on the role of Fe-concentration on the catalytic performances has been attempted by computing specific activity, expressed as mol\textsubscript{N\textsubscript{2}}/(mol\textsubscript{Fe})$\cdot$s$^{-1}$ (Table 2, column 7). A decreasing trend in calculated values emerged as a function of iron concentration for all the Fe/HAP samples, in particular for the Fe/HAP\textsubscript{e} catalysts. This could be related to the different sitting and accessibility of Fe species. Indeed, it is reasonable to assume that increasing the amount of iron introduced on HAP, iron centres should be located not exclusively at the surface, but also in the bulk positions of HAP, thus reducing their exposure and accessibility. Catalyst acidity evaluation also strengthened this consideration, as higher number of acid sites was not determined on the iron catalysts at higher Fe-concentration (see next paragraph). Moreover, comparing the samples at similar Fe-loading, higher values of specific activity have been observed on samples prepared by deposition-precipitation and wetness impregnation. It can be deduced that a judicious degree of metal aggregation is beneficial for the NO\textsubscript{x} conversion. In any case, increasing the iron loading did not have positive consequences on de-NO\textsubscript{x} activity. Actually, an increase in iron concentration does not imply a higher exposure of active sites.

A full understanding of these catalytic results cannot prescind from a detailed characterisation in terms of iron nucleation and speciation. For this reason, a combination of Mössbauer and UV-DRS spectroscopies was used to investigate the nature, structure and aggregation of the iron species of the Fe/HAP catalysts.

Studies on Fe speciation in relation with catalytic activity of Fe/HAP

The Mössbauer spectra of the Fe/HAP\textsubscript{e} samples collected at room temperature (25°C) and their hyperfine parameters are reported in Figure S4 (a–c) and Table S2, respectively. All the spectra presented only two peaks in the central region, so the fitting was realised using two doublets. In any case, low values of the isomer shifts (δ) were detected, typical of Fe\textsuperscript{3+} species. The doublets of all the three Fe/HAP\textsubscript{e} samples with lower isomer shifts (Table S2), which correspond to red lines in Figure S4 (a–c), have quadrupole splittings (Δ) significantly higher than the other doublets, corresponding to blue lines in Figure S4 (a–c). Both doublets could be produced by: (i) very small iron oxides crystallites with superparamagnetic behaviour, the doublet with higher Δ value could be assigned to iron ions located in the shell of the nanoparticles (with a surrounding highly asymmetric) and the other to iron ions located inside the core of the nanoparticles; or (ii) paramagnetic Fe\textsuperscript{3+} ions exchanged with Ca\textsuperscript{2+} ions and/or complexed by surface phosphate/carbonate groups. In this case, the iron ions exchanged would produce two doublets with different Δ values due to the non-equivalent sites of Ca\textsuperscript{2+} (Ca(1) and Ca(2)), exchangeable and with different symmetries, present on the HAP lattice.

With the aim to discern between both alternatives, Mössbauer spectra of Fe/HAP\textsubscript{e} samples were collected at −260.15°C (13 K) (Figure S5, a–c). Also in this case, all the spectra presented a central signal with two peaks. However, at −260.15°C the superparamagnetic relaxation of iron oxides nanoparticles should be totally or partially blocked, thus a sextuplet or a curved background must be present in the spectra. Consequently, it can be deduced that all catalysts prepared by flash ionic exchange procedure, independently of the Fe-loading, have high concentration of paramagnetic Fe\textsuperscript{3+} ions that replaced to the Ca\textsuperscript{2+} ions and/or complexed by surface phosphate/carbonate groups. As already done for the spectra at room temperature, the fitting was realized using two doublets. Jiang et al.$^{[8]}$ presented a theoretical and experimental study of the HAP exchanged with Fe\textsuperscript{3+} and Fe\textsuperscript{3+} ions and they demonstrated that the Fe\textsuperscript{3+} ions can replace both Ca(2) and Ca(1) ions. Bearing in mind the HAP structure,$^{[9]}$ the surrounding of the sites Ca(2) is more symmetric than that corresponding to Ca(1). This different geometry would explain the difference between Δ values of the two doublets (Table 3). This hyperfine parameter reflects the symmetry of the site where the iron atoms are located. A greater asymmetry produces a higher electric field gradient and, as a consequence, a greater Δ value.

The quantitative evaluation of the population of both sites was realized at −260.15°C (13 K) (Table 3) because the areas of both calculated doublets at 25°C have important errors, due to the high overlapping of the two doublets. Then, considering
that the difference between the recoil free fractions of both sites are negligible at very low temperatures, it can be concluded that the Ca(1) site is preferentially occupied by Fe$^{3+}$ ions (ratio of about 1.5), according to Ref. [20] and this ratio did not change when the iron loading is increased from 2 to 7 wt.%. These interesting results confirm the high exchange capability of the HAP: it is possible to functionalize it up to 7 wt.% of iron without having iron oxide nanoparticles, this in agreement with what reported in Refs. [21–22].

With the aim to check the absence of iron oxides compounds by an independent technique, a measure of magnetization (M vs. H) at room temperature of Fe7/HAP$_{IE}$ was performed (Figure S5). A straight line was obtained up to external magnetic field of 20 kOe. This magnetic behaviour is characteristic of paramagnetic materials. This result reinforces the conclusion that the only iron species are present as isolated Fe$^{3+}$ ions. From fitting the experimental points, the slope of the straight line leads to a magnetic susceptibility value ($\chi_g$) of $1.05 \times 10^{-4}$ emu · (g · Oe)$^{-1}$. The same conclusion could be obtained with the other samples which have lower iron loadings.

Figure 4. NH$_3$-SCR catalytic results on Fe/HAP samples prepared by flash ionic exchange (a–b), deposition-precipitation (c–d) and incipient wetness impregnation (e–f): comparison of NO$_x$ conversion as a function of reaction temperature at different ammonia concentrations (NH$_3$/NO = 1, green and NH$_3$/NO = 2, red).
Concerning the samples prepared by deposition-precipitation and wetness impregnation, different results were obtained. On two samples prepared by impregnation, it was observed that both Mössbauer spectra and the hyperfine parameters collected at room temperature (Figure S4, f–g, and Table S2, respectively) are very similar to those of Fe/HAP\textsubscript{IE} samples, while the situation was different for the spectra collected at \(-260.15^\circ\text{C}\) (13 K) (Figure 5, f–g). In order to facilitate the discussion, the Fe7/HAP\textsubscript{WI} sample will first be analysed. The spectrum of this sample showed a pronounced broadening of the central signal with a curved background, typical of the presence of species with a partial magnetic blocking. For this reason, the fitting process was approached with a relaxing sextuplet and two doublets (green and blue and red lines, respectively). It must be emphasized that, if the iron ions are in extremely small oxide particles, the resulting magnetic moment does not remain fixed in the space. Instead of this, it can be “jumping” between two easy magnetic directions. The fre-
quency of this “jumping” depends on the size of the nanoparticles, the temperature of the measurement, the iron oxide species, etc. Therefore, the sextuplet can collapse, following different line shapes which will depend on the frequency of the “jumping” of the magnetic moment. In the present samples the relaxing sextuplet has collapsed to a broad central singlet (Figure 5, f and g, green interaction). Previous reports of the literature indicate that amorphous iron oxide nanoclusters of about 4 nm size produce, at 268.15 °C (5 K), hyperfine parameters very similar to those found for the sextuplet (green line in Figure 5g). The hyperfine parameters do not depend strongly on the temperature, when sufficiently low temperatures were reached. Therefore, the obtained parameters at 260.15 °C (13 K) can be compared with that given by Bedeker et al. at 268.15 °C (5 K) and it can be concluded that a fraction of iron species in Fe7/HAP_w would be present as amorphous iron oxide. However, if the features of the spectrum showed by these authors are compared with the spectrum of Fe7/HAP_w at 260.15 °C (13 K), it can be seen that their clusters, of about 4 nm, are almost completely magnetically blocked. On the opposite, in Fe7/HAP_w, a very wide central signal and a curved background (green line in Figure 5g) only appear. This results would indicate the presence of nanoclusters with size lower than 4 nm because the magnetic blocking process is beginning at this point. Moreover, amorphous iron oxide nanoclusters of about 2 nm show, fundamentally, a super-paramagnetic behaviour at −268.15 °C (5 K) and a temperature as low as −273.07 °C (0.08 K) is necessary to get the complete magnetic blocking. Therefore, it could be concluded that about 70% of the iron loading in Fe7/HAP_w is present as amorphous iron oxides nanoclusters larger than 2 nm and smaller than 4 nm, because they have a higher magnetic blocking degree in comparison with what reported by Baumann et al. The remaining iron loading is exchanged and/or coordinated in the same way that in the samples prepared by flash ionic exchange (red and blue interactions of Figure 5a-c). For Fe5/HAP_w the same fitting procedure was followed but, the percentage of amorphous iron oxides nanoclusters is significantly decreased with respect to Fe7/HAP_w (30 ± 3% vs. 73 ± 3%, for Fe5/HAP_w and Fe7/HAP_w respectively, Table 3). Therefore, the wetness impregnation procedure does not allow reaching exchanged iron levels as high as that obtained by the flash ionic exchange method. Thus, when the HAP is loaded with 5% of iron, the clustering is already detected.

The Mössbauer spectra collected at room temperature of the two Fe/HAP_w samples showed only a central doublet (Figure S4, d-e). On the other hand, the spectra collected at 260.15 °C (13 K) were completely different: they clearly presented six peaks with an additional central peak and a background slightly curved (Figure 5, d-e). This could be related to the presence of iron oxides species with different magnetically blocking degrees. Therefore, the fitting was performed with three sextuplets: two of them almost completely magnetically blocked and the remaining just partially blocked. The hyperfine parameters of the sextuplet with the higher magnetic field (associated with red lines in Figure 5) are typical of α-Fe2O3 without Morin transition (2e=±0 mm/s-1). This is a magnetic transition that happens at −8.15 °C (265 K) when bulk hematite changes from an antiferromagnetic state (below −8.15 °C (265 K)) to a weakly ferromagnetic state (above −8.15 °C (265 K)) but it does not occur in nanoparticles of α-Fe2O3 which size is lower than 20 nm. Therefore, it is possible to determine that in both catalysts this species has a size lower than 20 nm. Another effect widely reported in literature for very small magnetic crystals of diverse iron oxides is the decreasing of the hyperfine magnetic field with respect to the corresponding bulk values present. Moran and Topsøe developed a model named collective magnetic excitations, which allows to explain decreasing of magnetic hyperfine fields from 5 to 15% with

| Table 3. Mössbauer parameters of Fe/HAP samples collected at −260.15 °C (13 K). |
|----------------|----------------|----------------|----------------|----------------|
| Code           | ΔH [mm·s^{-1}] | ΔE [mm·s^{-1}] | 2E0 [mm·s^{-1}] | H [kOe]       |
| Fe2/HAP_w      | 1.5 ± 0.1      | 0.55 ± 0.03    | –               | 38 ± 6        |
| Fe5/HAP_w      | 1.4 ± 0.1      | 0.52 ± 0.02    | –               | 62 ± 6        |
| Fe7/HAP_w      | 1.33 ± 0.07    | 0.51 ± 0.01    | –               | 39 ± 6        |
| Fe5/HAP_op     | 1.33 ± 0.04    | 0.51 ± 0.01    | –               | 61 ± 6        |
| Fe7/HAP_op     | 1.33 ± 0.04    | 0.51 ± 0.01    | –               | 61 ± 6        |
| Fe5/HAP_wi     | 1.76 ± 0.05    | 0.49 ± 0.02    | –               | 36 ± 6        |
| Fe7/HAP_wi     | 1.63 ± 0.05    | 0.52 ± 0.02    | –               | 12 ± 2        |
| Fe5/HAP        | 1.76 ± 0.05    | 0.49 ± 0.02    | –               | 36 ± 6        |
| Fe7/HAP        | 1.63 ± 0.05    | 0.52 ± 0.02    | –               | 12 ± 2        |

[a] Quadrupole splitting, [b] Isomer shift (all the isomer shifts are referred to α-Fe at 25 °C), [c] Quadrupole shift, [d] Hyperfine magnetic field, [e] Normalized population of Fe^{3+} centres, [f] Parameter held fixed in fitting.
respect to bulk compounds.\textsuperscript{[24]} Using this model\textsuperscript{[26]} and a value of anisotropic magnetic basal constant of $2.37 \times 10^4$ J m$^{-3}$, characteristic of hematite nanoparticles of about 6 nm,\textsuperscript{[30]} a rough size of the $\alpha$-Fe$_2$O$_3$ nanoparticles present in Fe/HAP$_{op}$ catalysts can be obtained; the value calculated in this way is ca. 4.5 nm. This size is consistent with the fact that this species was not detected by XRPD. The second sextuplet (associated with blue lines in Figure 5) can be assigned to nanoclusters of amorphous Fe$_2$O$_3$ by comparison with the results described by Badker et al.\textsuperscript{[31]} and using similar arguments than for Fe7/HAP$_{op}$. The features of the second sextuplet for Fe5/HAP$_{op}$ and Fe7/HAP$_{op}$ are very similar to that reported by these authors for iron oxide nanoclusters of about 4 nm. Therefore, this iron oxide fraction should have a higher size than that represented by the relaxing sextuplets (green lines in Figure 5f–g) in Fe5/HAP$_{ab}$ and Fe7/HAP$_{op}$. This conclusion is coherent with a higher magnetic blocking degree showed by the iron nanoclusters in Fe5/HAP$_{op}$ and Fe7/HAP$_{op}$. The third sextuplet (associated with green line in Figure 5d–e) of the two Fe/HAP$_{op}$ samples show a very similar shape to that present in Fe5/HAP$_{op}$ and Fe7/HAP$_{op}$ at $-260.15°C$ (13 K). Therefore, following the same arguments, this sextuplet can be attributed to amorphous iron oxide nanoclusters lower than 4 nm and higher than 2 nm.

Finally, all the prepared Fe/HAP samples have been analysed by UV-Vis-DR spectroscopy to confirm the results suggested by Mössbauer spectroscopy concerning iron speciation on HAP surface.

The UV-Vis DR spectra of all Fe/HAP samples were recorded at room temperature in the 200–1200 nm range; they are displayed in Figure 6 limited to the 200–800 nm region. Differen absorption bands typical of iron species were observed in this region and they can be ascribed to ligand-to-metal charge transfer (CT) excitations, from O (2p) nonbonding valence bands to Fe (3d) ligand field orbitals ($O^2−$ → Fe$^{3+}$), or to Fe$^{3+}$–d–d (ligand field) transitions. All the spectra were characterised by an apparent complexity due to the overlapping of different signals; therefore, the decomposition in sub-bands has been pursued to identify the different contributions.

In general, all the spectra are dominated by two features: \textit{i}) strong absorption in the 250–280 nm range, assigned to the CT transitions, due to the presence of isolated Fe$^{3+}$ centres, and \textit{ii}) broad absorption in the 460–550 nm range, corresponding to d–d transitions from ground state ($A_1$) to excited ligand field states ($\bar{T}_1$ or $\bar{T}_2$ or $\bar{E}$) (Table S3). In general, as the d–d transitions are spin forbidden, they are characterized by weak intensity, while more intense bands could be observed if iron clusters in some aggregate form are present, in which the magnetic coupling occurs between adjacent Fe$^{3+}$ ions.\textsuperscript{[32]} However, the attribution of these bands at high wavelength (> 400 nm) is debated in the literature where they have been attributed to d–d or CT transitions of Fe$_2$O$_3$ oligomers on several iron exchanged zeolites.\textsuperscript{[33,34]}

Moreover, another band at ca. 200 nm was observed in all the Fe/HAP spectra that could be assigned to $O^2−$–Ca$^{2+}$ charge transfer excitations, typical of Ca$^{2+}$ sites located on the HAP surface; this band is particularly visible in the spectra of the Fe/HAP$_{wi}$ series samples and on bare HAP (Figure 6).

Interestingly, the UV-Vis-DR spectra of all Fe/HAP$_{op}$ and Fe/HAP$_{ab}$ possessed more intense d–d transition bands than the spectra of the Fe/HAP$_{c}$ samples. This evidence confirms the high dispersion of the Fe-phase, predominantly present as isolated Fe$^{3+}$ centres with very limited aggregation, of the Fe/HAP$_{c}$ samples, and the presence of some Fe$_2$O$_3$ aggregates of the Fe/HAP$_{op}$ and Fe/HAP$_{ab}$ samples, as observed from Mössbauer spectroscopy. The detailed spectroscopic attributions for the samples are reported in Table S4.

The evaluation of the reducibility of different iron species present in the materials represents a powerful tool helping to establish meaningful relations between the variegated iron speciation in the Fe/HAP samples and the corresponding catalytic behaviour in the NH$_3$-SCR reaction, which is governed by electron exchanges. Temperature programmed reduction experiments (H$_2$–TPR) have been carried out to investigate the reduction behaviour of the Fe-phase of the Fe/HAP samples. TPR profiles and characteristic features (maximum temperatures of hydrogen consumption and H$_2$/Fe molar ratios) are reported in Figure S5 and Table 4, respectively. It is known that the reduction of iron species can occur according to different pathways including several intermediate steps. In addition the reducibility of iron centres strongly depends on the crystallite size and on the interactions with the support. This intrinsic complexity makes

| Table 4. | H$_2$–TPR results on Fe/HAP samples. |
|----------|-----------------------------------|
| Code     | Fe concentration [mmol·g$_{cat}$]$^{-1}$ | $T_{max}$ [°C] | $H_2$ consumption [mmol·g$_{cat}$]$^{-1}$ | H$_2$/Fe molar ratio |
| Fe2/HAP$_{op}$ | 0.37 | 472 | 0.09 | 0.25 |
| Fe5/HAP$_{op}$ | 0.85 | 455 | 0.21 | 0.24 |
| Fe7/HAP$_{op}$ | 1.22 | 485 | 0.36 | 0.29 |
| Fe5/HAP$_{ab}$ | 0.76 | 376 | 0.98 | 1.3 |
| Fe7/HAP$_{ab}$ | 1.13 | 374 | 1.37 | 1.2 |
| Fe5/HAP$_{wi}$ | 0.90 | 460 | 1.26 | 1.4 |
| Fe7/HAP$_{wi}$ | 1.25 | 373 | 1.49 | 1.2 |

(a) Temperature at peak maximum obtained from computation (Figure S7).
difficult any tentative attribution of TPR signals of our samples. Nevertheless, the information deriving from Mössbauer and UV-DR spectroscopies together with the literature results can help in interpreting the obtained profiles. In particular, the samples prepared by ion exchange procedures exhibit small peaks in the region between 470 and 550 °C, corresponding to a very low \( \text{H}_2 \) consumption. These signals could be ascribed to the reduction of isolated Fe\(^{3+} \) centres to...
Fe$^{2+}$. It is noteworthy that the same signals are individuated in the samples prepared by incipient wetness, even if additional reduction peaks are present in these catalysts at higher temperature. These results confirm the spectroscopic evidences, which suggest that incipient wetness method can lead in part to isolated centres and in part to iron oxide aggregates. Differently, these reduction peaks are not present in the samples prepared by deposition precipitation procedure. In this case, the presence of reduction peaks below 450°C (at ca. 375 and 400°C) may be consistent with the presence of large Fe$_2$O$_3$ aggregates, which are easily reduced to Fe$_3$O$_4$ and then to stable FeO species. These TPR signals below 450°C are also present in the samples prepared by wetness impregnation, thus supporting again the speculation from Mössbauer results, which indicates the presence of Fe$_2$O$_3$ aggregates in these samples.

The sample prepared by deposition-precipitation possessed the most reducible species (likely large Fe$_2$O$_3$ aggregates), in terms of hydrogen consumption (H$_2$/Fe molar ratio of ca. 1.2–1.4). On the contrary, ion exchange procedure produced iron samples characterized by a low reducibility (H$_2$/Fe molar ratio of ca. 0.2).

Conclusions

In this work, three different preparative methods (flash ionic exchange, deposition-precipitation and wetness impregnation) have been investigated for the preparation of Fe/HAP samples along with the effect of iron loading and both influenced the final aggregation states and the nature of iron species.

The catalytic behaviour resulted to be affected by the iron accessibility onto HAP surface. In particular, a very low amount of Fe on HAP (ca. 2 wt.%) is sufficient to impart de-NO$_x$ activity to HAP, whereas further Fe-addition (5–7 wt.%) does not induce a proportional improvement on the catalytic performances. Likely, a reduced accessibility of iron centres, which are not exclusively located at the HAP surface is responsible of the modest contribution of high Fe-loading.

Actually, the predominant presence of Fe$^{3+}$ highly dispersed on HAP surface on samples prepared by ionic exchange assured a high selectivity to N$_2$ and a satisfactory activity in a large temperature interval. The prevalence of iron aggregates on HAP caused a not negligible formation of N$_2$O as main product of the unselective ammonia oxidation occurring at temperature higher than 350°C.

In conclusion, the optimization of iron dispersion on the HAP surface seems to be a suitable route to follow for the achievement of active and selective Fe/HAP catalysts for the NH$_3$-SCR process. Further investigations will be devoted to the study of these materials under real conditions (presence of water and sulfur).

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Conflict of Interest

The authors declare no conflict of interest.

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