

Hydroxyapatite: A Matrix for Metal Exsolution Leading to Highly Dispersed Catalytically Active Species

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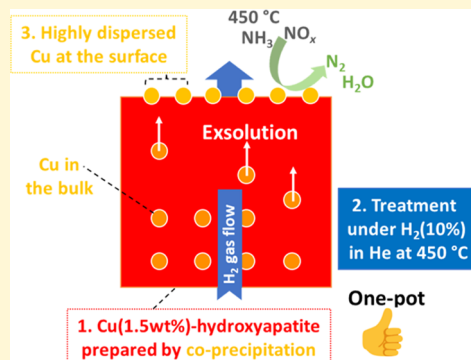


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ABSTRACT: Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ or HAp)—the main mineral component of bones and teeth—is a material of great interest not only in biomedical applications but also in heterogeneous catalysis. Its framework Ca^{2+} cations can be substituted by a wide variety of catalytically active metals (Cu^{2+} , Ni^{2+} , Ag^+ , etc.). In the present work, for the first time, to our knowledge, we demonstrate that highly valuable HAp-based catalysts can be obtained through a novel advantageous bottom-up approach. Unlike classical surface cation deposition in the excess of solution, this approach is one-pot. It consists in preparing the bulk-metal-substituted HAp by coprecipitation and then submitting it to a finely adjusted thermal treatment under a H_2 -containing gas flow. For a Cu (~1.5 wt %)-HAp, we show that such a treatment at 450 °C leads to the exsolution of the whole Cu contained in the material, leading to highly dispersed Cu species at the HAp surface. After appropriate activation, these Cu species are active in the selective catalytic reduction of NO_x by NH_3 . The phenomenon of exsolution has been reported so far mainly for perovskites but to lead to metal nanoparticles and not to highly dispersed species as achieved here.



1. INTRODUCTION

Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ or HAp) is a biocompatible and ecological material. As the main mineral component of bones and teeth, it can be obtained from natural sources, or it can be synthesized in mild conditions from cheap precursors.^{1–3} Besides playing an important role in many clinical applications such as drug design and bone tissue regeneration,⁴ it has proved to be efficient as a support and (co)active phase in heterogeneous catalysis.^{1,3,5–7} It has important advantages over other materials used in the latter field. Its specific surface area is higher than that of perovskites,^{8,9} while its thermal and chemical stabilities are generally better than those of zeolites and metal–organic frameworks.^{1,10,11} Its intrinsic surface acid–base properties can easily be tuned by varying its Ca/P ratio,^{12–14} and its framework Ca^{2+} cations can be substituted by catalytically active metals (Cu^{2+} , Ni^{2+} , Ag^+ , etc.).^{1,3,15} This leads to multifunctional catalysts suitable for a wide range of applications.^{1,3,5} Through surface cation deposition in the excess of solution or strong electrostatic adsorption (SEA), at substituent metal contents of 1–2 wt %, it is possible to obtain HAp catalysts with atomically dispersed active sites showing a particularly high catalytic performance and an exceptional resistance to sintering under harsh reaction conditions.^{16–18}

In the present work, for the first time, to our knowledge, we demonstrate that such highly valuable HAp-based catalysts with highly dispersed active sites can actually be obtained through an advantageous novel bottom-up approach. Unlike

surface cation deposition in the excess of solution, this novel approach is one-pot. It involves a phenomenon called “exsolution” that was first reported over perovskites.¹⁹ The latter phenomenon consists in the migration of metals incorporated on bulk sites of the perovskite toward the surface under a reducing atmosphere at temperatures above 800 °C. It leads to metal nanoparticles with a size depending on the latter temperature, which are socketed on the perovskite surface and thus unable to agglomerate.¹⁹ In the case of metal-substituted phosphates ($(\text{Sr or Ca})_{10-x}\text{M}_x(\text{PO}_4)_6(\text{OH})_2$ with M being the Sr^{2+} - or Ca^{2+} -substituting metal), the possibility of metal migration from the bulk toward the surface was briefly suggested in earlier studies of Yoon and co-workers.^{20–22} In these works, Ni-calcium phosphate, Ni-HAp, and Ni-strontium phosphate catalysts prepared by coprecipitation were progressively heated from 400 to 800 °C under a partial oxidation of methane (POM) reaction flow ($\text{CH}_4 + \text{O}_2/\text{Ar}$). Based on transmission electron microscopy (TEM) images and associated energy-dispersive spectroscopy before and after reaction, the authors concluded that Ni came out of the bulk of

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Table 1. Prepared Cu-HAp Samples^a

Sample	Post-synthesis thermal treatment		Cu weight content (%)	(Ca+Cu)/P bulk atomic ratio	Specific surface area (m ² /g)
	(1) Cleaning	(2) Reducing			
Cu-HAp(A)	Under Ar at 500 °C for 1.5 h	-	1.5	1.65	91
Cu-HAp(B)			1.2	1.66	84
Cu-HAp(C)			1.6	1.66	88
Cu-HAp(A) 450-1		Under H ₂ (x%)/He	1.5	1.65	99
Cu-HAp(A) 450-12			1.5	1.65	94
Cu-HAp(B) 600-12			1.2	1.66	55

^aFor one and the same Cu-HAp synthesis procedure, name of the different samples with respect to the conditions of the thermal treatment(s) applied following the synthesis, as well as Cu weight content (%) and (Ca + Cu)/P bulk atomic ratios assessed by ICP-OES and specific surface area (m²/g) assessed through N₂ physisorption. For the thermal treatments, samples were heated from room temperature to treatment temperature at (1) 5 °C/min and (2) 10 °C/min. The total flow rates were (1) 100 mL/min and (2) 50 mL/min. For treatment (2), the indicated H₂ content (x %) was introduced at room temperature.

the catalysts under reaction conditions, leading to Ni metal particles of a few nanometers at the surface. With increasing temperature, the reaction flow had been progressively enriched with H₂ produced from the POM reaction, indeed. However ultimate evidence of such an exsolution phenomenon exclusively in the Ni-HAp phases, namely, the migration of bulk Ni species toward the surface of Ni-HAp under a reducing atmosphere, is difficult to ascertain from the data shown in these studies.^{20–22} The presence of multiple phases, XRD-detectable or not, in these materials greatly complexifies the unraveling of the exsolution phenomenon unequivocally. In particular, the presence of small NiO particles, of which the TEM contrast with the supporting phosphate phase should be much lower than that of corresponding Ni metal particles, either could not be ruled out²¹ or was evidenced through TEM.²² These NiO particles may be at the origin of the “fine” Ni metal particles observed through TEM after the POM reaction,^{21,22} without the involvement of Ni exsolution. In addition, Ni-surface enrichment after the POM reaction could not be ascertained by XPS because of (i) the overlapping of the Sr 3d and P 2p contributions²⁰ and (ii) the fact that no significant difference could be found on the spectra of the Ni–Ca phosphate sample before and after the POM reaction.²² Here, in the case of Cu(~1.5 wt %)-HAp materials prepared by coprecipitation, through a combination of surface and bulk characterization techniques, we thoroughly demonstrate that Cu exsolution occurs under a reducing treatment at only 450 °C, and we assess the extent of that Cu exsolution. We further show that unlike in the case of perovskites where exsolution leads to nanoparticles at elevated temperatures,²³ the Cu exsolution from Cu-HAp results in highly dispersed Cu at the HAp surface. We finally show how to activate the exsolved Cu for catalyzing the selective catalytic reduction of NO_x by NH₃ (NH₃-SCR), a reaction of great interest for pollution control.^{24,25} Exsolving Cu is one step; making it available to act as a catalyst appears to be another step.

2. EXPERIMENTAL SECTION

2.1. Sample Preparation. Cu-HAp with the nominal composition Ca₅Cu₁(PO₄)₆(OH)₂ was prepared by coprecipitation in an automated reactor (Optimax 1001 synthesis workstation, Mettler Toledo) equipped with integrated pH meter, temperature sensor, and mechanical stirrer with adjustable speed, which offers the possibility to add the precursors solutions at a controlled speed.⁸

Calcium–copper and phosphate solutions were prepared by dissolving 11.54 g of Ca(NO₃)₂·4H₂O (Sigma-Aldrich, purity ≥99.0%) with 1.32 g of Cu(NO₃)₂·2.5H₂O (Sigma-Aldrich, purity ≥99.99%) in 250 mL of ultrapure water and 3.74 g of NH₄H₂PO₄ (Acros Organics, purity ≥99.0%) in another 250 mL of ultrapure water, respectively. 200 mL of the latter phosphate solution was then first adjusted to pH 10 by adding a small volume of concentrated ammonia solution (Sigma-Aldrich, 28%) before being poured into the reactor and maintained under an inert atmosphere (N₂). This phosphate solution was then gradually heated up to 80 °C (5 °C/min) under mechanical stirring (400 rpm). Its pH was continuously adjusted to 9 by dropwise adding concentrated ammonia. 200 mL of the calcium–copper solution, beforehand degassed by bubbling N₂ for about 15 min and adjusted to pH 10 by adding a few drops of concentrated ammonia, was then poured at a controlled speed (2.2 mL/min) into the reactor. During this step, the pH was kept at 9 by automatically adding appropriate volumes of concentrated ammonia. Once the addition step was completed, a 2 h maturation step at 80 °C and pH 9 was performed. The reactor temperature was finally cooled to 20 °C within a few minutes. The blue precipitate was recovered by centrifugation (8500 rpm) and washed three times with distilled water to mainly remove ammonia and ammonium and nitrate ions. The wet paste was then recovered on a watch glass and dried overnight at room temperature before the resulting solid was finely ground in an agate mortar.

The recovered Cu-HAp powder was treated under Ar (100 mL/min) at 500 °C (5 °C/min from room temperature) for 1.5 h. As described in Table 1, the samples that were not later additionally treated under H₂/He are named hereafter Cu-HAp(A), Cu-HAp(B), and Cu-HAp(C) with respect to the synthesis batch from which they originate (A, B, or C, respectively). The samples that were later additionally treated under H₂(10%)/He at 450 °C for 1 or 12 h or under H₂(20%)/He at 600 °C for 12 h are named hereafter Cu-HAp(A) 450-1, Cu-HAp(A) 450-12, and Cu-HAp(B) 600-12, respectively. The Cu-HAp(A) 450-1 and Cu-HAp(A) 450-12 samples

originate from the synthesis batch A, whereas the Cu-HAp(B) 600-12 sample originates from the synthesis batch B. The synthesis batch C was used for catalytic tests in the selective catalytic reduction of NO_x by NH_3 (Section 2.3).

2.2. Physicochemical Characterization. The actual Cu, Ca, and P weight contents of the prepared Cu-HAp were assessed by inductively coupled plasma optical emission spectroscopy (ICP-OES) with an Agilent 5100 SVDV spectrometer. Samples were mineralized typically as follows. 50 mg of powder was digested with 1 mL of HNO_3 (65% Normatom) at 80–90 °C during 4–6 h and then diluted in 50 mL of ultrapure water. 1 mL of the latter solution was finally diluted by adding HNO_3 (2%) until obtaining a total volume of 10 mL. For each analysis, three replicates were performed. Blanks were analyzed to monitor instrument and digestion procedure contamination. Standard solutions were prepared from multi-elemental and mono-elemental standards (SCP Science) and analyzed for calibration and quality control (drift, reproducibility and accuracy). The concentration of each element (Cu, Ca, and P) was calculated as the average of the data recorded at 2 to 5 different wavelengths (for Cu: 213.598, 223.009, 224.700, 324.754, and 327.395 nm; for Ca: 315.887 and 317.933 nm; for P: 178.222 and 213.618 nm).

The specific surface area was evaluated through N_2 physisorption at –196 °C on a BELSORP-max instrument (BEL Japan). Before measurement, the samples were degassed overnight under vacuum (about 10.66 Pa) at 150 °C. The specific surface area was evaluated from the Brunauer–Emmett–Teller (BET) equation ($0.05 < P/P_0 < 0.30$).

Ex situ X-ray diffraction (XRD) under air at room temperature was performed on a Bruker D8 Advance diffractometer equipped with a copper source ($\lambda_{\text{Cu-K}\alpha_1} = 1.54056 \text{ \AA}$ and $\lambda_{\text{Cu-K}\alpha_2} = 1.54439 \text{ \AA}$) and a LYNXEYE detector. Patterns were recorded in the 2θ range from 15 to 90°, with a step size of 0.02° and a time/step of 0.5 s.

Raman spectra were recorded on a DXR Thermo Scientific spectrometer coupled to an Olympus microscope using a 50 μm slit. A small amount of powder was deposited on a glass slide and flattened with another slide. The slide was then placed on the microscope worktable for analysis. The samples were excited at 532 nm with a laser power of 10 mW through a microscope objective set at a magnification of 50 $\times$. The estimated spectral and spatial resolutions were 5.5–8.3 cm^{-1} and 1 μm , respectively.

In situ XRD under He or H_2 (10%)/ He (30 mL/min) between room temperature and 450 °C was performed on a Bruker D8 Advance diffractometer equipped with a copper source ($\lambda_{\text{Cu-K}\alpha_1} = 1.54056 \text{ \AA}$ and $\lambda_{\text{Cu-K}\alpha_2} = 1.54439 \text{ \AA}$), an Anton Paar XRD 900 reactor chamber, and a LYNXEYE XE-T detector. Patterns were recorded in the 2θ range from 20 to 55°, with a step size of 0.02° and a time/step of 1 s (28.3 min/pattern). The source was operated at a power of 1200 W (40 kV, 30 mA).

X-ray photoelectron spectroscopy (XPS) was performed on an Omicron Argus spectrometer equipped with a monochromatic $\text{AlK}\alpha$ radiation source ($h\nu = 1486.6 \text{ eV}$) and an electron beam power of 280 W. Photoelectron emission was analyzed at a photoelectron collection angle of 45° under ultrahigh vacuum conditions ($\leq 10^{-9}$ mbar). The general spectrum was measured with a pass energy of 100 eV. Regarding the individual elements, the spectra were measured with a pass energy of 20 eV. The area of the C 1s, O 1s, P 2p, and Ca 2p peaks was determined with a linear background, and that of the Cu 2p peak was determined with a U2 Tougaard background. The atomic ratio calculations were performed after normalization using Scofield factors.²⁶ Spectrum processing was carried out using the Casa XPS software package. In order to determine the standard deviation of the calculated atomic ratios, one sample was analyzed at three different spots (whereas all of the other samples were analyzed at one single spot).

Cycles of temperature-programmed reduction (TPR) under H_2 (5%)/ He (25 mL/min), followed by temperature-programmed oxidation (TPO) under O_2 (5%)/ He (25 mL/min) were performed on an AutoChem 2910 instrument. The sample (100 mg) was pretreated *in situ* under O_2 (5%)/ He (25 mL/min) at 500 °C (10 °C/

min from room temperature) for 1 h. TPR and TPO experiments were typically performed by heating the sample from room temperature to 450 °C at 10 °C/min and then keeping it at 450 °C for 2 h (unless otherwise mentioned) before cooling it back to room temperature.

High-resolution transmission electron microscopy (HR-TEM) was carried out using a JEOL 2100 Plus UHR microscope operating at 200 kV. The powdered samples were dispersed in ethanol, and then, a drop was evaporated on a carbon-coated molybdenum grid. Scanning transmission electron microscopy (STEM) images using a high-angle annular dark-field (HAADF) detector were also acquired. The image contrast in this mode is strongly correlated with the atomic number: heavier elements contribute to brighter contrast (Z-contrast). Analytic investigations were performed with an energy-dispersive X-ray (EDX) spectrometer attached to the microscope column.

2.3. Catalytic Tests in the Selective Catalytic Reduction of NO_x by NH_3 (NH_3 -SCR). The catalytic activity of the prepared Cu-HAp in the selective catalytic reduction of NO_x by NH_3 (NH_3 -SCR) was investigated in a “Sandwich” reactor cell.²⁷ The pelletized Cu-HAp (2 cm^2 area, ~20 mg) was heated under Ar (30 mL/min) from room temperature to 450 °C (3 °C/min set heating rate) for 12 h. H_2 (10%) was added to the flow either 2 or 12 h before the end of the dwell time at 450 °C. In any case, following the reducing step at 450 °C, the sample was cooled down to 110 °C under H_2 (10%)/Ar (30 mL/min) and then flushed under Ar (30 mL/min) at 110 °C before being exposed to a flow of O_2 (20%)/Ar (30 mL/min) at 110 °C for 1 h. The sample was then heated to 120 °C (1 °C/min) under Ar (30 mL/min) and re-exposed to a flow of O_2 (20%)/Ar (30 mL/min) at 120 °C for 1 h.²⁵ Finally, after having been flushed under Ar (30 mL/min) at 120 °C, the sample was exposed to the reaction mixture from 120 to 450 °C (3 °C/min set heating rate with 1 h stops every 50 °C). The reaction mixture consisted of 500 ppm NO , 500 ppm NH_3 , and 1% O_2 in Ar (30 mL/min total flow rate).

Before sending the reaction flow to the reactor cell, the reactants were monitored by mass spectrometry (Quadrupole Pfeiffer Omnistar GSD 301) until their signals were stable. Then, under reaction conditions, the concentration of NO_x (NO and NO_2) in the outlet gas flow was analyzed by chemiluminescence (Thermo Scientific, model 42 i-HL). The conversion of NO_x was calculated from eq 1, where $(\text{NO}_x)_{\text{inlet}}$ and $(\text{NO}_x)_{\text{outlet}}$ are the NO_x concentrations at the inlet and outlet of the reactor, respectively.

$$\text{NO}_x \text{ conversion (\%)} = \frac{(\text{NO}_x)_{\text{inlet}} - (\text{NO}_x)_{\text{outlet}}}{(\text{NO}_x)_{\text{inlet}}} \times 100 \quad (1)$$

It was beforehand checked on another setup²⁸ that NO does not undergo significant direct decomposition (without the simultaneous conversion of NH_3) within the range of reaction temperatures investigated in the present work.

3. RESULTS AND DISCUSSION

3.1. Identity of the Prepared Cu-HAp Samples. Table 1 shows the ICP-OES-measured Cu weight content (%) and (Ca + Cu)/P bulk atomic ratio, as well as the specific surface area (m^2/g) assessed through N_2 physisorption, of the prepared Cu-HAp samples. The latter are named with respect to the synthesis batch from which they originate and to the conditions of the thermal treatment(s) applied following the synthesis.

All three Cu-HAp batches (A, B, and C) have similar Cu weight contents (1.5, 1.2, and 1.6%, respectively) and a (Ca + Cu)/P bulk atomic ratio of 1.65–1.66 characteristic of the HAp structure.⁸ The latter structure was also confirmed by the *ex situ* XRD patterns recorded under air at room temperature before and after the thermal treatments (Figures S1 and S2, respectively). These patterns are all matching with the 9-432-ICDD-PDF standard pattern of HAp, without showing additional signals of Cu-containing secondary phases (for

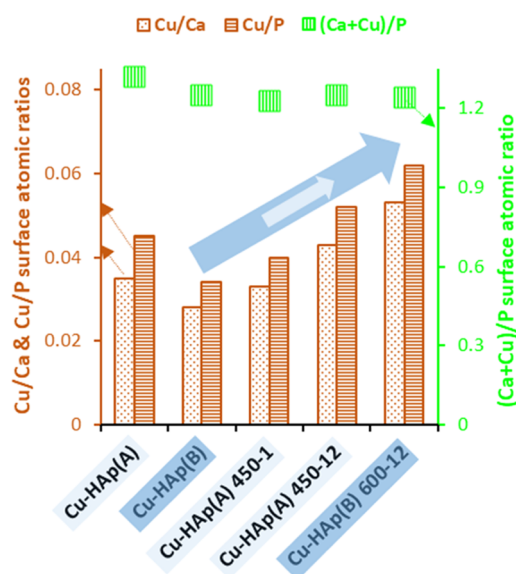


Figure 1. XPS-measured Cu/Ca, Cu/P, and (Ca + Cu)/P surface atomic ratios of Cu-HAp samples differing by the postsynthesis thermal treatment(s) they have undergone. The standard deviations corresponding to each of these three ratios are 0.0009, 0.0006, and 0.049, respectively, as determined by analyzing the Cu-HAp(B) sample at 3 different spots. All samples were first treated under Ar (100 mL/min) at 500 °C (5 °C/min from room temperature) for 1.5 h. The Cu-HAp(A) 450-1, Cu-HAp(A) 450-12, and Cu-HAp(B) 600-12 samples were later additionally treated under H₂ (10–20%)/He at 450 °C for 1 or 12 h or at 600 °C for 12 h, respectively, as further detailed in Table 1.

instance, libethenite—Cu₂PO₄(OH)—reported elsewhere²⁹). The partial substitution of Ca²⁺ cations (100 pm diameter) by smaller Cu²⁺ ones (73 pm diameter) in the here applied synthesis procedure does not induce a shrinkage of the HAp lattice that is sufficiently marked to make the HAp XRD pattern significantly shift to higher angles. In the concerned *ex situ* XRD patterns, slight shifts due to the experimental error (different sample holders, slightly different sample heights following sample preparation) prevail. This is why only *in situ* XRD experiments (Section 3.2), in which the experimental error is minimized by monitoring changes as a function of the sample treatment without ever renewing the sample preparation, are commented here in relation with Cu exsolution. The latter phenomenon potentially induces an expansion of the HAp lattice, indeed. The crystallite sizes determined from the *ex situ* XRD patterns by using the Debye–Scherrer equation for the (002), (222), and (213) diffraction lines (Tables S1–S3) are essentially unaffected by the reducing treatments at 450 °C. In the case of the (222) and (213) diffraction lines, the treatment at 600 °C slightly increases the calculated crystallite size (18.5 nm for Cu-HAp(B) 600-12 vs 15.8 nm for Cu-HAp(B) and 19.7 nm for Cu-HAp(B) 600-12 vs 16.3 nm for Cu-HAp(B), respectively). The presence of other apatite phases did not appear from Raman spectroscopy, which revealed no significant difference between the six Cu-HAp samples of Table 1 (spectra in Figures S3–S5).

The homogeneous distribution of Cu within the material was checked through STEM-EDX analyzes both before and after the reducing treatment at 600 °C (Figures S6 and S7). The fact that the actual Cu weight contents (1.2–1.6%) are lower than the nominal one (6.5%, corresponding to the nominal composition Ca₉Cu₁(PO₄)₆(OH)₂) is attributed to

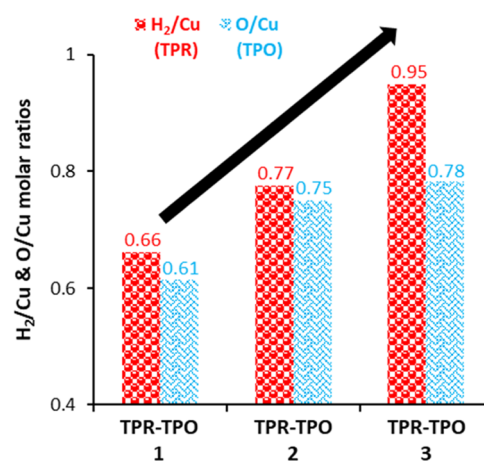


Figure 2. For three successive cycles of temperature-programmed reduction (TPR)–temperature-programmed oxidation (TPO) on the same Cu-HAp(A) sample, molar ratios of H₂ consumed over Cu contained in the sample (H₂/Cu) and O consumed over Cu contained in the sample (O/Cu). The sample (100 mg) was beforehand treated *ex situ* under Ar (100 mL/min) at 500 °C (5 °C/min from room temperature) for 1.5 h and then *in situ* under O₂(5%)/He (25 mL/min) at 500 °C (10 °C/min from room temperature) for 1 h. TPR and TPO experiments were then alternately performed under H₂(5%)/He (25 mL/min) and O₂(5%)/He (25 mL/min), respectively. Each TPR experiment was immediately followed by a TPO one before the next TPR experiment was performed. In each TPR/TPO experiment, the sample was heated from room temperature to 450 °C at 10 °C/min and then left under the reduction or oxidation flow for another 2 h, except in the last TPO experiment. The latter consisted of heating the sample up to 900 °C (10 °C/min) without stop at 450 °C.

the formation of [Cu(NH₃)₄]²⁺ complexes during the synthesis upon adding NH₄OH to adjust the pH. The Cu-HAp(A), Cu-HAp(B), and Cu-HAp(C) samples have similar specific surface areas (91, 84, and 88 m²/g, respectively). The reducing treatments at 450 °C do not significantly affect the specific surface area (99 and 94 m²/g after the 1 h- and 12 h-treatment, respectively, vs 91 m²/g before treatment). The reducing treatment at 600 °C reduces the specific surface area (55 m²/g vs 84 m²/g before treatment). For all samples, the N₂ adsorption–desorption isotherms are provided in Figures S8 and S9.

3.2. Demonstration of Cu Exsolution Leading to Highly Dispersed Cu Species. Figure 1 shows the XPS-measured Cu/Ca, Cu/P, and (Ca + Cu)/P surface atomic ratios of the Cu-HAp(A), Cu-HAp(B), Cu-HAp(A) 450-1, Cu-HAp(A) 450-12, and Cu-HAp(B) 600-12 samples defined in Table 1. The raw XPS spectra are provided in Figures S10–S14.

The (Ca + Cu)/P surface atomic ratios (~1.3) appear to be significantly lower than those expected from the bulk composition of the materials (1.65–1.66, Table 1). This discrepancy may be assigned to differences in surface composition of the HAp materials, with the preferential exposure of phosphate groups rather than Cu²⁺ and/or Ca²⁺ cations, as compared to the bulk composition.⁶ The Cu-HAp(A) 450-1 sample has lower (Ca + Cu)/P, Cu/Ca, and Cu/P surface atomic ratios than the Cu-HAp(A) one originating from the same synthesis batch (A) but not having been treated under H₂/He (1.23, 0.033, and 0.040 vs 1.32, 0.035, and 0.045, respectively). This reflects the creation of

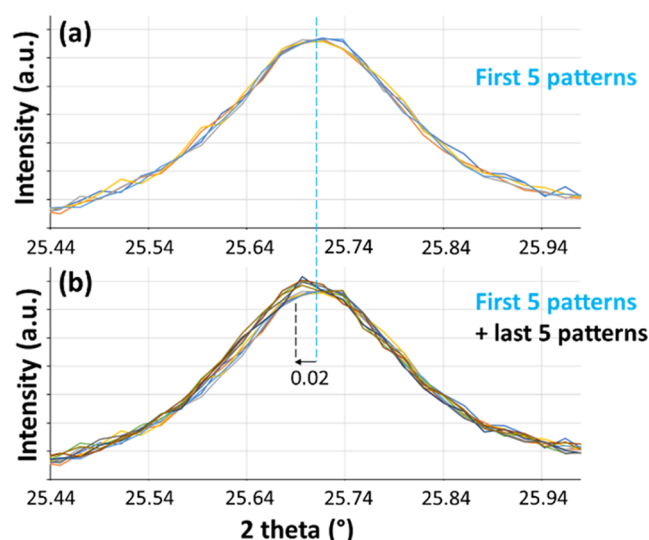


Figure 3. *In situ* XRD patterns of the Cu-HAp(A) sample at 450 °C under $\text{H}_2(10\%)/\text{Ar}$ (30 mL/min) for 12 h, in the region of the (002) diffraction line. The sample—beforehand treated under Ar (100 mL/min) at 500 °C (5 °C/min from room temperature) for 1.5 h—was heated from room temperature to 500 °C under He (30 mL/min), at 3 °C/min with 45 min stops every 50 °C. The sample was then cooled to 450 °C and first kept overnight under He (30 mL/min) before being finally exposed to the flow of $\text{H}_2(10\%)/\text{Ar}$. The XRD patterns were measured successively during the first 2.5 h (first 5 patterns in panels (a) and (b)) and the last 2.5 h (last 5 patterns in panel (b)) under $\text{H}_2(10\%)/\text{Ar}$. Each pattern was measured from 20 to 55°, with a step size of 0.02° and a time/step of 1 s (28.3 min/pattern).

structural defects under reducing treatment. Interestingly, while the Cu-HAp(A) 450-1 and the Cu-HAp(A) 450-12 samples—treated under $\text{H}_2(10\%)/\text{He}$ at 450 °C for 1 and 12 h, respectively—have nearly the same (Ca + Cu)/P surface ratio (1.23 vs 1.25, respectively), the Cu-HAp(A) 450-12 sample has significantly higher Cu/Ca and Cu/P surface ratios than the Cu-HAp(A) 450-1 one (0.043 and 0.052 vs 0.033 and 0.040, respectively). This indicates that within the additional 11 h of treatment under $\text{H}_2(10\%)/\text{He}$ at 450 °C to which the Cu-HAp(A) 450-12 sample was submitted, the surface of the latter was Cu-enriched and Ca-depleted. This in turn suggests that Cu^{2+} cations migrated from the Cu-HAp bulk toward the surface, with Ca^{2+} migrating at the opposite from the Cu-HAp surface into the bulk. In other words, Cu exsolution occurs with time upon treating a Cu(1.5 wt %)-HAp under $\text{H}_2(10\%)/\text{He}$ at 450 °C.

An even higher increase of the Cu/Ca and Cu/P surface ratios is observed from the Cu-HAp(B) sample to the Cu-HAp(B) 600-12 one (0.028 and 0.034 vs 0.053 and 0.062, respectively), at a nearly constant (Ca + Cu)/P ratio (1.25 vs 1.24, respectively). Both samples originate from the same synthesis batch (B), but only the Cu-HAp(B) 600-12 sample was treated under H_2/He (at 600 °C for 12 h). The Cu-HAp(B) 600-12 sample ends up with higher Cu/Ca and Cu/P ratios than the Cu-HAp(A) 450-12 sample (0.053 and 0.062 vs 0.043 and 0.052, respectively), while both samples have nearly the same (Ca+Cu)/P ratio (1.24 vs 1.25, respectively). This increase of Cu/Ca and Cu/P ratios from the Cu-HAp(A) 450-12 sample to the Cu-HAp(B) 600-12 one appears even more significant considering that the counterpart of Cu-HAp(B) 600-12 before reducing treatment (Cu-HAp(B)) has lower

Cu/Ca and Cu/P ratios than the counterpart of Cu-HAp(A) 450-12 before reducing treatment (Cu-HAp(A)) (0.028 and 0.034 vs 0.035 and 0.045, respectively). It indicates that Cu exsolution occurs to a higher extent under $\text{H}_2(20\%)/\text{He}$ at 600 °C than under $\text{H}_2(10\%)/\text{He}$ at 450 °C. To distinguish between the impacts of the H_2 concentration and the treatment temperature was not the goal here.

The data of TPR-TPO cycles applied to the Cu-HAp(A) sample are also consistent with Cu exsolution from the Cu-HAp structure under prolonged reducing treatment. These data further allowed quantifying the extent of exsolution in the considered temperature range. Figure 2 shows the molar ratios of H_2 consumed over Cu contained in the sample (H_2/Cu) and O consumed over Cu contained in the sample (O/Cu) in three successive TPR-TPO cycles on the same Cu-HAp(A) sample. The sample (100 mg) was pretreated *in situ* under $\text{O}_2(5\%)/\text{He}$ (25 mL/min) at 500 °C (10 °C/min from room temperature) for 1 h. TPR and TPO experiments were then alternately performed under $\text{H}_2(5\%)/\text{He}$ (25 mL/min) and $\text{O}_2(5\%)/\text{He}$ (25 mL/min), respectively. Each TPR experiment was immediately followed by a TPO one before the next TPR experiment was performed. In each TPR/TPO experiment, the sample was heated from room temperature to 450 °C at 10 °C/min and then left under the reduction or oxidation flow for another 2 h, except in the last TPO experiment. The latter consisted of heating the sample up to 900 °C (10 °C/min) without stop at 450 °C. The H_2 and O_2 consumption profiles as a function of temperature are provided in Figure S15. The different H_2 and O_2 consumption signals (Figure S15a,b, respectively) were quantified vs time as one whole amount of H_2 and O_2 consumed, respectively. It was then considered that every 1 mol of H_2 consumed had reduced 1 mol of Cu^{2+} into Cu^0 and that every 1/2 mol of O_2 consumed had reoxidized 1 mol of Cu^0 into Cu^{2+} .^{30,31} Note that on the TPR profile of a non-Cu-substituted HAp sample prepared and pretreated in the same conditions as the Cu-HAp(A) sample (Figure S16), the H_2 consumption is negligible in the here considered temperature range (room temperature to 450 °C, Figure S16a). The only H_2 consumption peak of weak intensity appears at 490 °C (Figure S16b) and may be attributed to H_2 adsorption on an acid–base pair such as $\text{Ca}^{2+}-\text{O}^{2-}$, as hydride and proton species.³²

The H_2/Cu molar ratio of 0.66 resulting from the first TPR experiment (TPR-TPO cycle 1 in Figure 2) indicates that 66% of the whole Cu^{2+} initially contained in the sample was reduced into Cu^0 within the first TPR. A very close fraction of Cu^0 (61%) was then reoxidized into Cu^{2+} in the subsequent TPO (still TPR-TPO cycle 1 in Figure 2). Such a high fraction of Cu reduced and then reoxidized cannot result from the only reduction/oxidation of $\text{Cu}^{2+}/\text{Cu}^0$ at the surface of the sample. Cu from the bulk must have been additionally involved. From the first to the second TPR-TPO cycle, the H_2/Cu and O/Cu molar ratios increase to 0.77 and 0.75, respectively. This indicates that the second TPR-TPO experiment led to the reduction/oxidation not only of Cu^{2+} that had already been reduced/oxidized in the first TPR-TPO cycle but also of an additional fraction of Cu species newly accessible to H_2/O_2 . The second TPR experiment comprised again a dwell time of 2 h at 450 °C, indeed, which pushed the process of Cu exsolution further. From the second to the third TPR-TPO cycle, only the H_2/Cu molar ratio further increases (from 0.77 to 0.95, respectively). The O/Cu ratio remains nearly the same (0.75 vs 0.78, respectively). Given that the HR-TEM images of

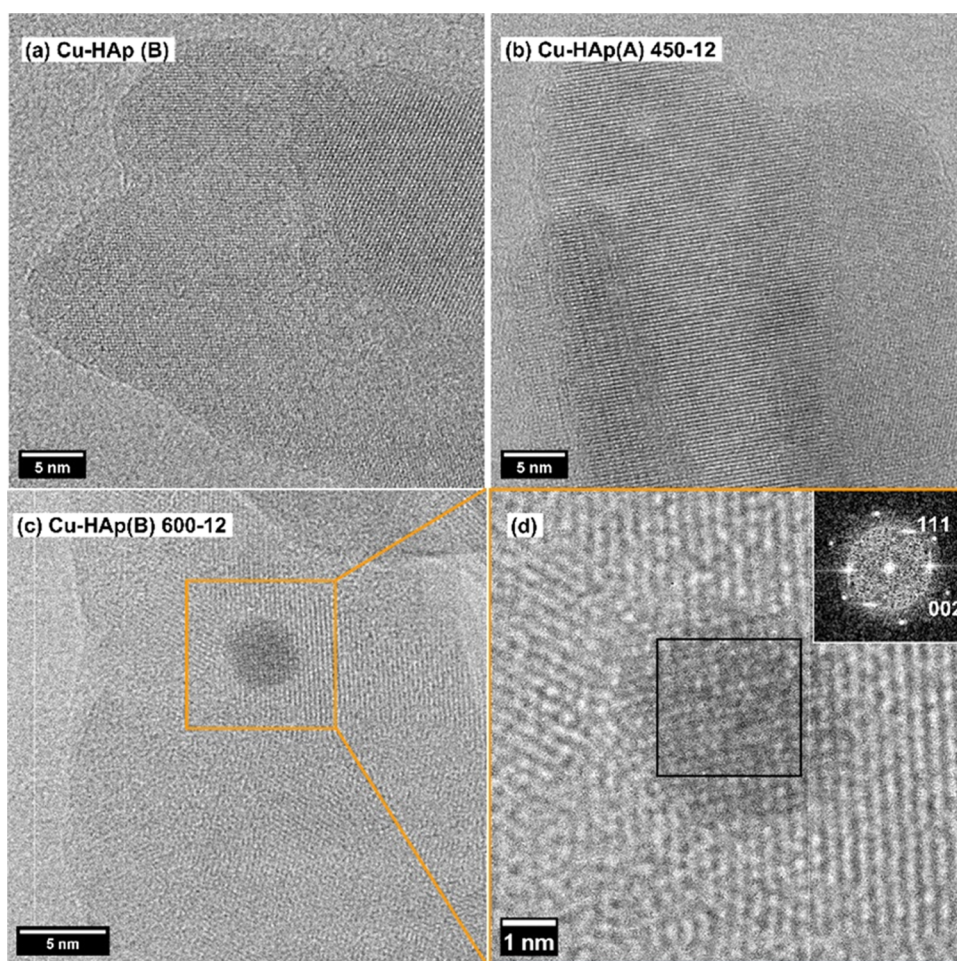


Figure 4. (a–d) HR-TEM images of three Cu-HAp samples having undergone different postsynthesis thermal treatment(s). In all cases, the samples were first treated under Ar (100 mL/min) at 500 °C (5 °C/min from room temperature) for 1.5 h. In panels (b) and (c), the samples were additionally treated under $\text{H}_2(x\%)/\text{He}$ (50 mL/min, with $x = 10$ and 20, respectively) at 450 and 600 °C (10 °C/min from room temperature), respectively, for 12 h (see definition of the sample names in Table 1). In panel (d), the inset shows the fast Fourier transform (FFT) of the black squared area.

Cu-HAp(A) 450-12 do not show Cu particles (Figure 4b), this feature cannot be explained by the exsolution of hardly oxidizable Cu^0 particles in the third TPR experiment. However, it might be ascribed to the fact that the Cu newly exsolved in the third TPR experiment remained in the deepest surface layers or in the near-surface bulk being still accessible to H_2 but not to O_2 . While the H_2/Cu ratio in the third TPR experiment (0.95, Figure 2) is already close to 1, suggesting a complete Cu exsolution, the Cu/Ca and Cu/P surface atomic ratios further increase from the Cu-HAp(A) 450-12 sample to the Cu-HAp(B) 600-12 one (Figure 1). This is consistent rather with the hypothesis of exsolved Cu trapped in the near-surface bulk after the reducing treatment at 450 °C.

From the point of view of the Cu-HAp bulk, the exsolution of Cu has a slight impact on the *in situ* XRD patterns of the Cu-HAp(A) sample under a 12 h exposure to $\text{H}_2(10\%)/\text{Ar}$ (30 mL/min) at 450 °C (Figure 3). The sample was heated from room temperature to 500 °C under He (30 mL/min), at 3 °C/min with 45 min stops every 50 °C. It was then cooled to 450 °C and first kept overnight under He (30 mL/min) before being finally exposed to the flow of $\text{H}_2(10\%)/\text{Ar}$ (30 mL/min) for 12 h. Figure 3 shows the XRD patterns that were recorded at 450 °C successively during the first 2.5 h (first 5 patterns in both Figure 3a,b, for clarity) and the last 2.5 h (last 5 patterns

in Figure 3b) under $\text{H}_2(10\%)/\text{Ar}$. Figure S17 shows the equivalent patterns recorded in the preceding step at 450 °C under He. All of these patterns are shown in the region of the (002) diffraction line which is the sharpest in the *ex situ* pattern of Cu-HAp(A) under air at room temperature (Figure S1a). As compared to the (002) diffraction line in the latter pattern, the (002) diffraction line in Figures 3 and S17 is centered at a slightly smaller angle due to thermal expansion (around 25.72° in Figures 3 and S17 vs 25.94° in Figure S1a). Such shifts due to thermal expansion are the only changes that were observed on the *in situ* XRD patterns recorded from room temperature to 500 °C under He (Figure S18).

At 450 °C under He (Figure S17), no significant change is observed between the first 5 and the last 5 *in situ* XRD patterns. At 450 °C under $\text{H}_2(10\%)/\text{Ar}$, on the last 5 patterns (Figure 3b), the maximum of the (002) diffraction line is slightly shifted (about 0.02°) toward smaller angles corresponding to a slightly expanded HAp lattice, as compared to the first 5 patterns (Figure 3a,b). Such an expansion of the HAp lattice evokes the above-concluded migration of $\text{Cu}^{2+}/\text{Ca}^{2+}$ toward the surface/bulk of the material, as Ca^{2+} cations are wider in diameter than Cu^{2+} ones (100 pm vs 73 pm, respectively). According to the TPR-TPO and XPS data (Figures 2 and 1, respectively), Cu exsolution from the Cu-

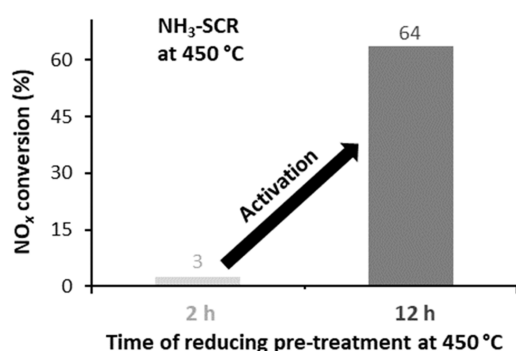


Figure 5. NO_x conversion at 450 °C (with a standard deviation of 0.05%, as calculated over 10 successive values at steady state) in two separate NH₃-SCR experiments on the Cu-HAp(C) sample (20 mg) as a function of the time for which this sample was pretreated *in situ* under H₂(10%)/Ar (30 mL/min) at 450 °C before being reoxidized *in situ* under O₂(20%)/Ar (30 mL/min) at 110 °C for 1 h and then at 120 °C for 1 h. The sample was finally exposed to the reaction mixture (500 ppm NO, 500 ppm NH₃, and 1% O₂ in Ar; 30 mL/min total flow rate) from 120 to 450 °C (3 °C/min set heating rate with 1 h stops every 50 °C). In both experiments, the reducing pretreatment consisted of heating the sample from room temperature to 450 °C (3 °C/min set heating rate) under Ar (30 mL/min) for 12 h. H₂(10%) was added to the flow either 2 or 12 h before the end of the dwell time at 450 °C. Before these NH₃-SCR experiments, the sample had already been treated *ex situ* under Ar (100 mL/min) at 500 °C (5 °C/min from room temperature) for 1.5 h.

HAp has indeed occurred to almost 100% after a total of only 6 h under H₂(5%)/He at 450 °C, with a minority fraction of the exsolved Cu being located in the near-surface bulk. In a comparable experiment with non-Cu-substituted HAp, no shift was observed over time at 450 °C under H₂(10%)/Ar (Figure S19).

Figure 4 shows HR-TEM images of the Cu-HAp(B) (Figure 4a), Cu-HAp(A) 450-12 (Figure 4b), and Cu-HAp(B) 600-12 (Figure 4c,d) samples.

The fact that no Cu particle appears on the Cu-HAp(A) 450-12 sample (Figure 4b) means that a full Cu exsolution at 450 °C leads to highly dispersed Cu species at the surface of the material. Cu particles were observed only for the Cu-HAp(B) 600-12 sample (Figure 4c,d) that was treated at a higher temperature than the Cu-HAp(A) 450-12 one (600 vs 450 °C, respectively) and under a higher concentration of H₂ (20 vs 10%, respectively). In Figure 4d, the fast Fourier transform (FFT) of the black squared area shows the characteristic pattern of metallic Cu.^{33,34} The FFT of a surrounding area, showing only the characteristic pattern of HAp, is provided in Figure S20. The identity of the Cu particles observed for the Cu-HAp(B) 600-12 sample was further confirmed by STEM-EDX mapping (Figure S21). Typical HR-TEM images of the Cu-HAp(B) 600-12 sample at a lower magnification are provided in Figures S22 and S23. The diameter of the Cu particles observed in these images ranges from 2.4 to 10.9 nm. No investigation of the particles size distribution is provided since the aim here is to focus on the conditions allowing to get a very high dispersion. The appearance of Cu particles on the Cu-HAp(B) 600-12 sample is not necessarily related only with Cu exsolution. At a reduction temperature as high as 600 °C, it can also result from the sintering of Cu that was already present at the surface of the material before the reducing treatment.

3.3. Activation of Exsolved Cu for Catalyzing the NH₃-SCR of NO_x. Reducing treatments at 450 °C as discussed above were performed also as pretreatments in NH₃-SCR experiments on the Cu-HAp(C) sample. More precisely, the sample was pretreated *in situ* under Ar then H₂(10%)/Ar (30 mL/min total flow rate) at 450 °C for 12 h before being reoxidized²⁵ *in situ* under O₂(20%)/Ar (30 mL/min) at 110 °C for 1 h and then at 120 °C for 1 h. The reoxidation step was required as Cu needs to be cationic to catalyze the NH₃-SCR.^{24,25} Two experiments were performed with different pretreatment times under H₂(10%)/Ar, namely, 2 h vs 12 h. Figure 5 shows the resulting NO_x conversion at 450 °C under a reaction mixture of 500 ppm NO, 500 ppm NH₃, and 1% O₂ in Ar (30 mL/min total flow rate).

As the pretreatment time under H₂(10%)/Ar increases from 2 to 12 h, the NO_x conversion in Figure 5 increases from 3 to 64% and thus by a factor of 21. On the other hand, in Figure 2, the H₂/Cu molar ratio has already reached 66% at the first TPR and then further increases only by a factor of 1.5, from 66 to 95%, from the first to the third TPR, i.e., as the total time under H₂(5%)/He at 450 °C increases from 2 to 6 h. Furthermore, in Figure S15b, the O₂ consumptions at 120 °C in the first to third TPO experiments are very close. Thus, based on the TPR-TPO data, a partial exsolution treatment of 2 h followed by a reoxidation at 120 °C should have led to about the same final amount of reoxidized catalytically active sites as a full exsolution treatment of 6 h or longer followed by the same reoxidation at 120 °C. This discrepancy between the NH₃-SCR and TPR-TPO data suggests that not all of the Cu that was reduced by H₂ in the TPR experiments (Figure 2) and then reoxidized at 120 °C (Figure S15b), of which the highest fraction resulted from Cu exsolution, was also immediately accessible to the whole reaction mixture (NO_x + NH₃ + O₂) in the NH₃-SCR experiment (Figure 5). Possibly a significant part of the Cu reduced/exsolved at 450 °C in the three successive TPR experiments that was reoxidized at 120 °C in the subsequent TPO experiments is actually located in deep surface layers where it is not available for converting NO_x by NH₃-SCR. The 12 h reducing pretreatment in the NH₃-SCR experiments makes the concerned exsolved Cu truly show-up at the surface, resulting in a significant NO_x conversion (Figure 5).

4. CONCLUSIONS

For the first time, to our knowledge, the present paper demonstrates through a combination of surface and bulk characterization techniques that a metal, here Cu, can exsolve from a bulk-metal-substituted HAp, here Cu(1.5 wt %)-HAp synthesized by coprecipitation. About 66% of the whole Cu initially contained in the Cu-HAp is exsolved after 2 h under H₂(5%)/He at a temperature as low as 450 °C; nearly 100% is exsolved after 6 h. A fraction of the exsolved Cu however remains in deep surface layers/the near-surface bulk of the material. Therefore, to become available for catalyzing reactions, this exsolved Cu might require a prolonged treatment. Here, in the NH₃-SCR of NO_x at 450 °C, the Cu exsolved after 2 h under H₂(10%)/Ar at 450 °C (at least 66% of the whole Cu initially contained in the material) is not immediately active following a reoxidation treatment. It becomes active, however, after prolonging the treatment under H₂(10%)/Ar at 450 °C to 12 h, followed by the same reoxidation treatment. The 12 h reducing treatment actually leads to a full Cu exsolution but keeping the exsolved Cu

surface species highly dispersed. Nanoparticles of Cu (2 nm < diameter < 11 nm) appear only after a reducing treatment at higher temperature and/or higher H₂ concentration, as observed for a Cu-HAp sample treated under H₂(20%)/He at 600 °C for 12 h.

The present work shows that reaching a 1.5 wt % surface content of highly dispersed Cu on HAp does not require a two-pot synthesis approach such as precipitation of the HAp, followed by Cu²⁺ deposition in the excess of solution. Such a surface content of highly dispersed Cu can be achieved through a one-pot synthesis approach, namely, coprecipitation of the Cu-HAp, followed by H₂-treatment for Cu exsolution. As this approach is *a priori* not restricted to only Cu as the catalytically active metal, the present work constitutes a considerable step forward in the development of efficient routes for the design of highly active HAp-based catalysts.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.chemmater.3c01749>.

Ex situ XRD patterns in the 2 θ region from 15 to 90° of all Cu-HAp samples under air at room temperature; crystallite sizes of all samples calculated by using the Scherrer equation for the (002), (222), and (213) diffraction lines; Raman spectra of all samples under air at room temperature; HR-TEM and STEM-HAADF images of the Cu-HAp(B) 600-12 sample with corresponding STEM-EDX maps; HR-TEM images of the Cu-HAp(B) 600-12 sample at a lower magnification for an overview of the size of Cu particles; STEM-HAADF image of the Cu-HAp(B) reference sample with corresponding STEM-EDX maps; N₂ adsorption-desorption isotherms for all Cu-HAp samples; XPS spectra of all samples; H₂ consumption and O₂ consumption profiles in three successive H₂-TPR-O₂-TPO cycles on the same Cu-HAp(A) sample; H₂ consumption profile in the TPR experiment performed on a non-Cu-substituted HAp sample; *in situ* XRD patterns of the Cu-HAp(A) sample upon heating from 30 to 500 °C under He and then upon keeping the sample overnight at 450 °C under He; and *in situ* XRD patterns of a non-Cu-substituted HAp sample at 450 °C under H₂(10%)/Ar (PDF)

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Notes

The authors declare no competing financial interest.

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