CATALYTIC PRODUCTION OF HYDROXYL RADICALS UNDER PHYSIOLOGICAL CONDITIONS

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Introduction

Reactive oxygen species (ROS) including superoxide ($\cdot O_2^-$), ozone (O_3), atomic oxygen (O), hydrogen peroxide (H_2O_2), hydroxyl radical (HO·) are known to have significant influences in biological systems [1,2]. Indeed, as by-products of normal intracellular metabolism, they play key physiological roles in cells and tissues and their controlled production could favour cell proliferation or differentiation [1,2] and therefore tissue regeneration. A way to control their production and to favour their reaction with bone (stem) cells would be to embed HO· radical production catalysts inside smart scaffolds. However, it is difficult to control catalysts size and structure within it. Our approach is then to incorporate iron catalysts in mesoporous silica particles, which could be embedded in smart scaffolds for bone regeneration. Indeed, inorganic nanoparticles incorporated in polymeric scaffold lead to their improvement [3]. The silica particles studied here will have several other useful functionalities, such as contrast agents and stimuli-responsive drug delivery.
In this study, the preparation and characterization of iron oxide catalysts on mesoporous silica particles to produce HO· radicals from H_2O_2 under physiological conditions is presented. It is shown that H_2O_2 can be efficiently converted into HO· radicals with such nanoparticles and the quantity of HO· radicals generated has been quantified and correlated to the catalysts characteristics.

Materials and Methods

Spherical MCM-48 particles were synthesized according a known procedure [4]. Hydrophobic magnetite nanoparticles (MNPs) were synthesized by co-precipitation and then coated with oleic acid [5], or by thermal decomposition of iron-oleate complex [6]. Hydrophilic MNPs were synthesized by using a 'two-step method' [7], where the MNPs are first synthesized and washed before being mixed with citric acid. Citrate-stabilized hydrophilic MNPs were also obtained following the procedure reported by Yang *et al.* [8]. The MCM-48 decoration by the MNPs was performed by first modifying the MCM-48 surface as described by Stoeva *et al.* [9], and the MNPs surface as described by Kim *et al.* [10], before reacting them together. MCM-48 decoration was also realised by synthesizing the NPs in its presence: MCM-48 (0.27 g) was added to $FeCl_3 \cdot 6H_2O$ (70 mg) and $FeCl_2 \cdot 4H_2O$ (26 mg) in 3.5 mL of deionized H_2O and stirred in an Ar atmosphere for 2 h. The mixture was heated to 90°C followed by rapid addition of ammonia solution (1 mL, 14 wt.%), and heating for a further 90 min. The mixture was cooled to RT and the solid isolated by filtration, washed with deionized H_2O and acetone, and dried under vacuum. A third way was impregnating MCM-48 with an aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$, under incipient wetness conditions (IWI). The impregnated powder was dried at 100°C (12 h), calcined at 500°C (5 h) and then reduced under hydrogen at 400°C. The powder catalysts were analysed by TEM with a LEO922 Omega Energy Filter Microscope operating at 120 kV. Room-temperature fluorescence spectra were recorded on a Varian Cary Eclipse instrument (excitation wavelength 346 nm).

Results and Discussion

The MCM-48 synthesised displayed a ~1278 m²/g specific surface area and homogeneous spherical structure (particle diameter between 270 and 530 nm). Different approaches were used to decorate MCM-48 with magnetite nanoparticles (MNPs). First, hydrophilic or hydrophobic MNPs (~10 nm) were synthesized according to various methods and anchored post-synthetically or prepared concomitantly to MCM-48 synthesis. Second, MCM-48 was also impregnated with a solution of $Fe(NO_3)_3 \cdot 9H_2O$ followed by calcination/reduction. The obtained Fe_xO_y/MCM-48 composite materials were characterized and then tested for the production of HO· radicals from H_2O_2. These tests were carried out in the presence of coumarin to follow the production of HO· radicals by fluorescence spectroscopy (FIG. 2).
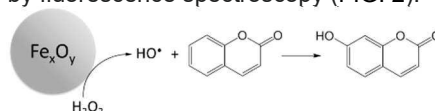

FIG. 2. Production of HO· from H_2O_2 on iron oxide catalyst and reaction between HO· and coumarin forming fluorescent 7-hydroxycoumarin.

This allowed us to discriminate our materials and select the most promising, which are those with smallest Fe_xO_y particles (< 2 nm). These small sizes are associated with amorphous particles. FIG. 2.a shows the results obtained with Fe_xO_y/MCM-48 presenting different iron loadings, which demonstrates the ability of our materials to produce HO· radicals. The TEM image visible in 2.b corresponds to the catalyst with the lowest iron loading.
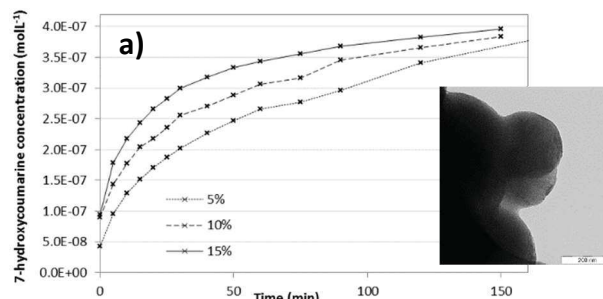

FIG. 2. (a) Kinetic and (b) TEM analysis of Fe_xO_y/MCM-48 catalyst with different wt.% iron loadings.

Conclusions

We have shown that iron-based catalysts are efficient for the production of HO· radicals from H_2O_2 in water at room temperature and we were able to follow this production over time by fluorescence spectroscopy.

Acknowledgments

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