

Letter

# Formation of radical oxygen species on hydroxyapatite

Yasuyuki Matsumura<sup>a,\*</sup>, Hiroyoshi Kanai<sup>b</sup>, John B. Moffat<sup>c</sup>

<sup>a</sup> Osaka National Research Institute, AIST, Midorigaoka, Ikeda, Osaka 563, Japan

<sup>b</sup> Faculty of Life Science, Kyoto Prefectural University, Simogamo, Sakyo-ku, Kyoto 606, Japan

<sup>c</sup> Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

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## Abstract

Hydroxyapatite of approximately stoichiometric composition (Ca/P molar ratio 1.65) evacuated at 600°C and exposed to O<sub>2</sub> at room temperature produces ESR spectra with  $g_{xx} = 2.0013$ ,  $g_{yy} = 2.0102$  and  $g_{zz} = 2.0160$ , providing evidence for the formation of O<sub>2</sub><sup>-</sup>. Although the ESR signal attributed to Fs<sup>+</sup> centers is observable on both nonstoichiometric apatite (Ca/P molar ratio 1.61) and the stoichiometric form, no change in the ESR signal of the former sample takes place after adsorption of oxygen at room temperature. The formation of O<sub>2</sub><sup>-</sup> suggests presence of O<sup>2-</sup> of low coordination in the stoichiometric form.

**Keywords:** Apatite; ESR; Radical oxygen; F center; Vacancy

## 1. Introduction

Hydroxyapatites [Ca<sub>10-2z</sub>(PO<sub>4</sub>)<sub>6-2z</sub>(HPO<sub>4</sub>)<sub>z</sub>(OH)<sub>2-2z</sub> (0 ≤ z ≤ 1)] have been shown to have catalytic properties which are dependent upon the molar Ca/P ratio, with the stoichiometric composition having properties as a basic catalyst while the nonstoichiometric form (Ca/P < 1.67) is acidic [1–5]. Hydroxyapatites are active for the catalysis of the partial oxidation of methane with oxygen to carbon monoxide and hydrogen being formed at 600°C in the initial stage of the reaction over both the stoichiometric and nonstoichiometric forms [6]. However, the selectivities to carbon monoxide and hydrogen produced with the two

forms are significantly different, the selectivity to carbon monoxide for the latter catalyst being higher than that for the former while the selectivity to hydrogen is lower. Since the difference in the catalytic activity may be related to the variation in acid–base properties, hydroxyapatite is an interesting compound for elucidation of the relation between acid–base sites and the reactivity to oxidation. In the present paper we have studied oxygen radical formation on hydroxyapatite and show decisive difference in the activation of oxygen between stoichiometric and nonstoichiometric apatites.

## 2. Experimental

Hydroxyapatites were prepared from Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (BDH AnalaR) and

\* Corresponding author. Fax: +81-727-519629.

$(\text{NH}_4)_2\text{HPO}_4$  (BDH AnalaR) according to the method described in Ref. [7]. The resulting solids were heated at  $500^\circ\text{C}$  for 3 h after drying at  $120^\circ\text{C}$  for 18 h. The Ca/P molar ratios of the approximately stoichiometric (Ap-S) and non-stoichiometric (Ap-N) samples were 1.65 and 1.61, respectively, determined by analyzing the concentrations of  $\text{Ca}^{2+}$  and  $\text{PO}_4^{3-}$  ions in the solutions remaining from the synthesis by ion chromatography.

ESR spectra were recorded with a JES-TE-300 spectrometer at 9.30 GHz at room temperature. The sample was placed in a quartz ESR tube in which preheating in vacuo at  $600^\circ\text{C}$  for 1 h and adsorption of oxygen at room temperature were carried out.

### 3. Results and discussion

After evacuation at  $600^\circ\text{C}$  some ESR lines were recorded with hydroxyapatites (Fig. 1). The lines can be separated into two set of signals. One is estimated as a triplet ( $g_{\parallel} = 2.0048$ ,  $g_{\perp} = 2.0051$ ,  $A_{\parallel} = 3.5$  mT, and  $A_{\perp} = 3.2$  mT for Ap-S, and  $g_{\parallel} = 2.0049$ ,  $g_{\perp} = 2.0053$ ,  $A_{\parallel} = 3.5$  mT, and  $A_{\perp} = 3.0$  mT for Ap-N) and the other is a broad singlet ( $g = 2.0035$  for Ap-S and Ap-N) which was reported by Monma et al. in hydroxyapatite pre-

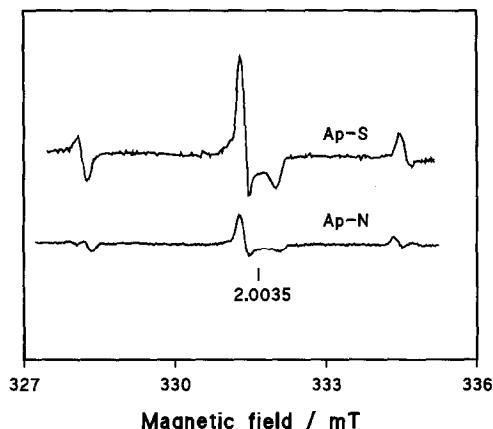


Fig. 1. ESR signals for hydroxyapatites evacuated at  $600^\circ\text{C}$ . Microwave power, 0.2 mW.

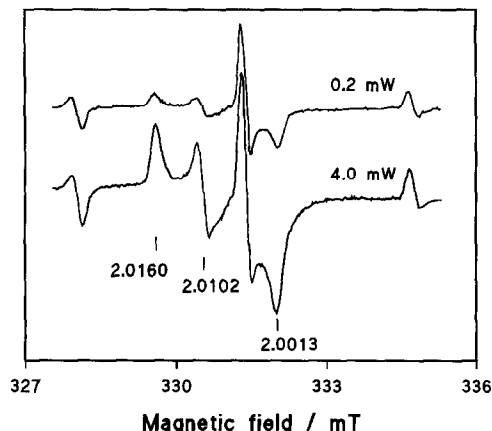


Fig. 2. ESR signals for Ap-S after adsorption of oxygen for 1 day at room temperature followed by evacuation for 1 min.

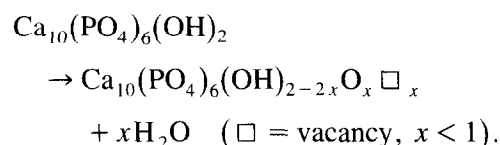
pared by the hydrolysis of tricalcium phosphate [8]. The  $g$ -values are close to that of an  $\text{Fs}^+$  center which results from an electron trapped in an oxygen vacancy [9,10]. The triplet was saturated at the microwave power of ca. 1 mW, but no saturation was observed for the singlet up to 4 mW. The intensities for the triplet peaks are 1:2:1, suggesting that there are two equivalent nuclear spins near the ESR center. It was reported that the proton causes hyperfine splitting of 0.2 mT to a surface center equivalent to F centers in bulk [11]. The splitting in the triplet is obviously larger than that due to the proton and, hence, the center is probably interposed between two  $^{31}\text{P}$  atoms.

New significant ESR lines appeared after adsorption of oxygen (13 kPa) on Ap-S followed by evacuation at room temperature for 1 min while the original lines remained. The intensities of the new lines gradually increase with the time for the adsorption, and the spectrum shown in Fig. 2 was obtained after the adsorption for 1 day. With increase in the microwave power, the new lines were emphasized and the signal was not saturated up to 9 mW. Simulation of the ESR peaks was carried out and the  $g$ -values were determined as  $g_{xx} = 2.0013$ ,  $g_{yy} = 2.0102$ , and  $g_{zz} = 2.0160$ , suggesting the radical species is  $\text{O}_2^-$  [12]. The  $g$ -values are also close to those for  $\text{O}_3^-$  radical [12]. However, the

ESR measurements with  $^{17}\text{O}$  enriched oxygen gave two sets of hyperfine structures, one with 11 lines and the other with 6 lines both with a hyperfine tensor of  $A_{xx} = 7.7$  mT, demonstrating the formation of  $^{17}\text{O}_2^-$  and  $^{16}\text{O}^{17}\text{O}^-$  both with equivalent oxygen nuclei, respectively, suggesting that the radical oxygen assumes a structure parallel to the surface on the adsorption site [12].

In contrast, no significant change in the ESR signal was observed on Ap–N after the adsorption of oxygen for 3 days, suggesting that the ESR centers originally present in apatite are not responsible for the formation of the  $\text{O}_2^-$  radical. The absence of  $\text{O}_2^-$  radicals on nonstoichiometric apatite may account for the difference in the catalytic activity in the methane oxidation from that observed with the stoichiometric form.

Cordischi et al. reported formation of  $\text{O}_2^-$  with three  $g$ -values ( $g_{xx} = 2.000$ ,  $g_{yy} = 2.007$ , and  $g_{zz} = 2.10$ ) on CaO evacuated at  $900^\circ\text{C}$  where the center responsible for the radical formation is probably  $\text{O}^{2-}$  in surface sites of low coordination [13]. In hydroxyapatite hydroxyl groups are stabilized in the columns containing calcium-ion triangles, but these groups transform into oxygen and vacant sites in the columns through dehydration of apatite at high temperatures, that is [14,15],



The formation of the vacancies can account for the presence of the ESR feature attributed to the  $\text{Fs}^+$  center. Hence the  $\text{O}^{2-}$  ions in the columns of stoichiometric apatite may be the centers responsible for the  $\text{O}_2^-$  formation. Since the  $g_{zz}$  value for  $\text{O}_2^-$  is sensitive to the effective crystal field around the adsorption site [14], the difference in  $g_{zz}$  values found for the stoichiometric apatite and calcium oxide may be related to the dissimilar locations of  $\text{O}_2^-$  in these solids. The slow formation of  $\text{O}_2^-$  will be caused by slow diffusion in the calcium-ion columns in which

distance between the calcium ions is only 0.4 nm. Although  $\text{HPO}_4^{2-}$  groups are formally present in nonstoichiometric apatite, they are apparently transformed into  $\text{P}_2\text{O}_7^{4-}$  at  $200^\circ\text{C}$  in the nonstoichiometric (Ca/P ratio, 1.61) apatite [6]. However, spectroscopic evidence for the existence of  $\text{P}_2\text{O}_7^{4-}$  in the nonstoichiometric apatite vanished after evacuation at  $600^\circ\text{C}$  [6]. Thus the absence of  $\text{O}_2^-$  radicals on the nonstoichiometric apatite may be attributed to the interaction of  $\text{O}^{2-}$  in the column and  $\text{P}_2\text{O}_7^{4-}$  producing two  $\text{PO}_4^{3-}$  groups and eliminating  $\text{O}^{2-}$  ions in the columns. Recent EXAFS studies on hydroxyapatite have shown that the mean distance of Ca–O in the structure increases with increase in the nonstoichiometry [16]. Since the Ca–O mean distance of the calcium found in the columns of hydroxyapatite is appreciably shorter than that found outside the columns [17], the calcium defects which are concomitant with  $\text{HPO}_4^{2-}$  and/or  $\text{P}_2\text{O}_7^{4-}$  are primarily present on the columns in nonstoichiometric apatite where the interaction between  $\text{P}_2\text{O}_7^{4-}$  and the  $\text{O}^{2-}$  ion may be possible.

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