

Formation of oxygen radicals by coordinatively unsaturated oxygen anions on hydroxyapatite

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Received 25 July 1997; revised 4 December 1997; accepted 12 December 1997

Abstract

Coordinatively unsaturated oxygen (O_{CUS}^{2-}) is generated on nonstoichiometric hydroxyapatite formally expressed as $Ca_{9.66}(PO_4)_{5.66}(HPO_4)_{0.34}(OH)_{1.66}$ by evacuation at 900°C. Interaction between O_2 and O_{CUS}^{2-} generated by the dehydration of the hydroxyl groups in the apatite results in the simultaneous appearance of ESR centers assigned as O_{CUS}^- (hole center) and O_2^- radical oxygen species, evidently showing that O_{CUS}^{2-} can donate electron to O_2 and activate it. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Hydroxyapatite; Oxygen radical; ESR; V-center; F-center

1. Introduction

Oxygen radicals on the surface of alkaline earth oxide, which is often employed for oxidation catalysts [1,2], have been detected by the electron spin resonance (ESR) technique [3–7]. The formation of O_2^- with three g -values ($g_{xx} = 2.000$, $g_{yy} = 2.007$, and $g_{zz} = 2.10$) on CaO evacuated at 900°C has been attributed to the interaction of coordinatively unsaturated oxygen anions (O_{CUS}^{2-}) with O_2 to form O_2^- radicals and O_{CUS}^- [6]. Although indirect evidence suggests the presence of coordinatively unsaturated oxygen [5–8], no ESR signals due to the center,

which should be paramagnetic, have been observed simultaneously with those for O_2^- , and this prevents exact understanding of the activation mechanism of oxygen, which is the key step in catalytic oxidation.

Hydroxy apatite [$Ca_{10-z}(PO_4)_{6-z}(HPO_4)_z(OH)_{2-z}$, $0 \leq z \leq 1$] catalyzes the oxidation of methane [9] and O_2^- radical ions can be detected by ESR on a stoichiometric hydroxyapatite evacuated at 600°C in which the Ca:P molar ratio is approximately 1.67 [10]. The formation of O_2^- appeared to be due to the presence of O_{CUS}^{2-} produced by dehydration of the structural hydroxy groups; however, no direct evidence was found for this supposition.

In the present study, the simultaneous formation of O_2^- and O_{CUS}^- on the nonstoichiometric apatite highly dehydrated at 900°C has been

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directly detected, while such species cannot be observed on the solid preheated at 600°C.

2. Experimental

Nonstoichiometric hydroxyapatite was prepared from $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (BDH AnalaR) and $(\text{NH}_4)_2\text{HPO}_4$ (BDH AnalaR) according to the method described in Ref. [11]. The resulting solids were heated at 500°C for 3 h after drying at 120°C for 18 h. The Ca:P molar ratio of the sample was 1.61, determined by analyzing the concentrations of Ca^{2+} and PO_4^{3-} ions in the solutions remaining from the synthesis by ion chromatography (Dionex 4500i).

ESR spectra were recorded at room temperature with a JES-TE-300 spectrometer at 9.30 GHz. The sample was placed in a quartz ESR tube in which preheating in vacuo at 900°C for 1 h and adsorption of oxygen at room temperature was carried out.

3. Results and discussion

Although ESR signals with g -values of approximately 2.005 attributed to one electron trapped in an oxygen vacancy (F-center) can be observed in hydroxyapatite evacuated at 600°C [10], no significant signal was recorded with the nonstoichiometric hydroxyapatite evacuated at 900°C for 1 h. After adsorption of oxygen (13 kPa) on this sample at room temperature for 2.5 h followed by evacuation for 1 min, complex ESR signals appeared in the range of 320–333 mT (solid curve in Fig. 1). After evacuation at room temperature for 4.5 h, the lines at 329–331 mT were obliterated, and the intensity of the line at 332 mT increased (solid curve in Fig. 2).

The formation of O_2^- with $g_{xx} = 2.0013$, $g_{yy} = 2.0102$, and $g_{zz} = 2.0160$ on a stoichiometric apatite evacuated at 600°C has been confirmed [11]. The signal at 329–331 mT in Fig. 1, which disappeared on evacuation at room temperature, is similar to that for O_2^- : the g -val-

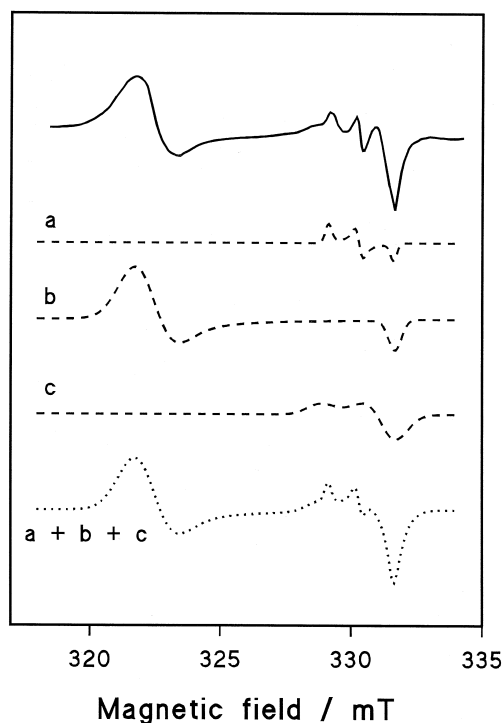


Fig. 1. ESR signals for radical oxygen species on nonstoichiometric hydroxyapatite evacuated at 900°C. Solid curve, observation; broken curves, simulation; dotted curve, sum of curves a–c.

ues ($g_{xx} = 2.003$, $g_{yy} = 2.0114$, and $g_{zz} = 2.0185$) were obtained by ESR simulation (Fig. 1a), while the line at 331.7 mT is overlapped by other ESR signals. Formation of O_2^- on alkaline earth oxides has been attributed to electron transfer from $\text{O}_{\text{CUS}}^{2-}$ to oxygen with consequent formation of O_{CUS}^- [4–7]. Although structural O^- radical centers (V-centers) on alkaline-earth oxide produced by X-ray irradiation were detected by ESR [3,12,13], this signal was not observed with O_2^- [4–7]. On the contrary, the g -value of the signal at 320–325 mT in Fig. 1b and Fig. 2a is approximately that for g_{\perp} for V-centers on calcium oxide ($g_{\perp} = 2.07$ and $g_{\parallel} = 2.002$) [3,12,13] and the shape of the signal is very similar to that observed with the O^- radical [14]. The g -values from ESR simulation are determined as 2.0628 (Fig. 1b) and 2.0645 (Fig. 2a) for g_{\perp} and 2.004 for g_{\parallel} the latter of which is also similar to that for the V-center [3,12,13]. Hydroxyapatite has a hexagonal crys-

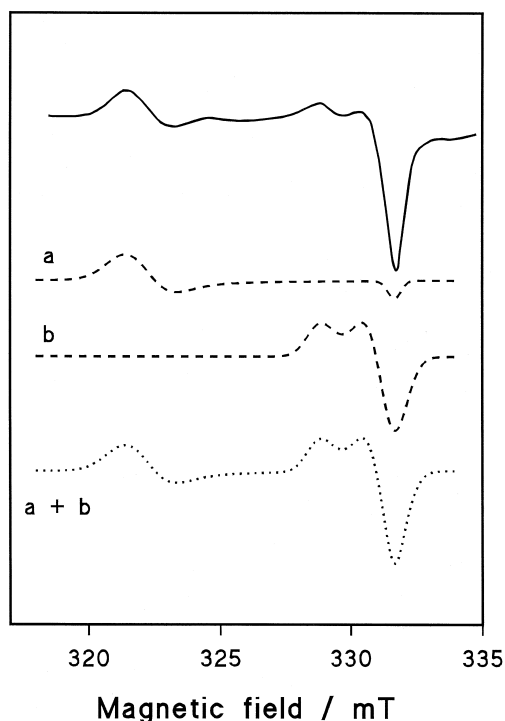
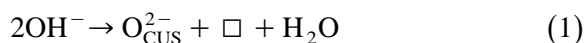


Fig. 2. ESR signals for nonstoichiometric apatite after adsorption of oxygen followed by evacuation for 7 h. Solid curve, observation; broken curves, simulation; dotted curve, sum of curves a and b.

tal structure constructed from narrow columns constituted from the layers of three-membered rings of calcium atoms (the distance between the atoms is 0.4 nm) [15]. Although hydroxy groups are stabilized in the columns, in the nonstoichiometric apatite, dehydration occurs at high temperature, that is,



where \square is an oxygen vacancy [16,17]. Interaction between oxygen and $\text{O}_{\text{CUS}}^{2-}$ results in the formation of O_2^- , that is,



Since these radical species are formally substituted to the hydroxyl groups, the distance of the radicals is supposed to be at least 0.34 nm while O_2^- may migrate to the other oxygen vacancy in the column [15].

As evident from Fig. 2 the intensity of the signal at 332 mT is larger than that in the simulation for this center (Fig. 2a). A broad peak is also present at 329 mT. This implies that another ESR center exists and the g -values are obtained as 2.005 for g_{\perp} and 2.0208 for g_{\parallel} from the simulation (Fig. 2b). The signal also exists in the spectrum for the sample containing O_2^- (Fig. 1c). The g -values are close to those of the V-centers found in zeolites after γ -irradiation in which the resulting structures are Si–O[−]–Si or Al–O[−]–Si [4,18,19]. The center can interact with oxygen and produce radical species attributed to O_3^- [4,19]. However, no change in the ESR spectrum was found after treatment of the evacuated sample with oxygen (13 kPa) at room temperature for 2.5 h followed by evacuation for 1 min, suggesting that the center is stable and O_2^- cannot be reproduced. It is also possible that the ESR centers may result from F-centers interacting with O_{CUS}^- in the narrow calcium column. The formation of the center can be explained as desorption of O_2^- from the oxygen vacancy, i.e.,



and F-centers formed in hydroxyapatite by evacuation at 600°C do not react with oxygen [10]. F-centers are usually isotropic; however, it should be anisotropic if the distance between the V-center and the F-center is close. The shape of the peak at 332 mT in Fig. 2, which is narrower than that simulated using Gaussian function, may suggest interaction between the two radical centers [20].

Acknowledgements

We cordially thank Professor Satohiro Yoshida of Kyoto University for providing the ESR simulator program. This work was partially funded by the Natural Sciences and Engineering Research Council of Canada to which our thanks are due.

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