ESR study of the active oxygen species on hydroxyapatite activated by heat treatment

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Abstract

The paper deals with the ESR study of the active oxygen radical ($O_2{}^-$) formed on the hydroxyapatite (HAP). The $O_2{}^-$ species were generated by heating HAP in vacuo at 973 K followed by treating with oxygen at room temperature. They smoothly reacted with propylene, methane, hydrogen and benzene at room temperature where the reactivity decreased in that order. When the $O_2{}^-$ species were reacted with propylene followed by heating in vacuo at 873 K for 1 h and treating with oxygen at room temperature, a quartet signal ($g = 2.002$, $a = 2.15$ mT, 1:3:3:1) was formed. It decayed by heating at 573 K for 10 min and restored again the original $O_2{}^-$ species with treatment of oxygen. The quartet lines were derived from the interaction of an unpaired electron with three equivalent phosphorus atoms. ESR spectra changed depending upon the temperature at which heating was applied on HAP after $O_2{}^-$ had been reacted with propylene. The behavior was attributed to the different active species for O_2 produced by the series of treatments: formation of $O_2{}^-$ on thermally activated HAP, reaction of the $O_2{}^-$ species with propylene, heating at 673–973 K and treatment with O_2.
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1. Introduction

Many types of oxygen species such as O^-, O^{2-}, $O_2{}^-$ and $O_3{}^-$ have been proposed as active species for oxidation reactions [1–3]. In the previous paper, we reported that hydroxyapatite (HAP) catalyzed partial oxidation of methane at 873 K [4]. ESR is a useful tool for studying active oxygen species [5,6]. We have focused on active oxygen species as the catalytically active species on HAP [4,7–10]. When HAP was heated in vacuo at higher than 873 K followed by treating with atmospheric oxygen at room temperature, $O_2{}^-$ was formed on HAP [8–10]. The species was relatively stable in the O_2 atmosphere or on standing without O_2 in the gas phase at room temperature [10]. The $O_2{}^-$ species reacted with propylene, methane, hydrogen and benzene at room temperature. Aliphatic olefins reacted rapidly with $O_2{}^-$, and methane and hydrogen reacted moderately. The $O_2{}^-$ ESR

signal was decayed for the reactions with propylene, methane and hydrogen, but a new signal appeared in the reaction with benzene. After the $O_2{}^-$ species on HAP was consumed and the HAP was heated in vacuo at 873 K for 1 h, fresh oxygen was treated at room temperature. Strikingly, quartet hyperfine lines appeared. On the other hand, when the HAP was heated in vacuo at 973 K followed by treating with O_2, $O_2{}^-$ was again produced. There was no quartet signal. The quartet signal was derived from the interaction between the newly produced unpaired electron and three equivalent phosphorus atoms.

We are pursuing the reactivity of oxygen species on HAP activated by heat treatment.

2. Experimental

Hydroxyapatite (HAP) was prepared from $Ca(NO_3)_2 \cdot 4H_2O$ (Nacalai tesque Co.) and $(NH_4)_2HPO_4$ (Nacalai tesque Co.) according to the general procedure[11]. The resulting solids were dried at 393 K for 12 h. Ethylene, propylene, methane and

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hydrogen were purchased from Takachiho Chemical and Industrial Co.

HAP (0.15 g) was placed in an ESR tube and heated in vacuo at 973 K for 2 h. The HAP was cooled to room temperature and oxygen (100 Torr) was added. After 3.5 h residual oxygen was evacuated and the ESR measurement was carried out at room temperature using a JEOL ESR spectrometer (JES-TE-300). An O_2^- signal was observed. Propylene (10 Torr) was reacted with O_2^- and the decay of the O_2^- signal was pursued at some intervals. The signal diminished rapidly and disappeared after 8 min. The HAP was heated at 673 K, 773, 873 and 973 K in vacuo for 1, 1, 1 and 0.5 h, respectively, followed by treating with O_2 (1 atm) in each run. An ESR spectrum was obtained at room temperature in each run.

3. Results and discussion

3.1. ESR spectra of O_2^- on the hydroxyapatite and its reactions with propylene, methane and hydrogen

After hydroxyapatite (HAP) was heated in vacuo at 973 K for 2 h followed by treating with oxygen at room temperature, an O_2^- signal ($g_1 = 2.017$, $g_2 = 2.011$, $g_3 = 2.003$) was obtained as shown in Fig. 1 [8–10]. The formation of O_2^- was assumed as follows [9]:

$$2OH^- \rightarrow O_{CUS}^{2-} + \square + H_2O \tag{1}$$

$$O_{CUS}^{2-} + O_2 \rightarrow O_2^- + O^- \tag{2}$$
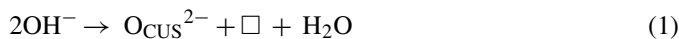
where $\square$ stands for an oxygen vacancy.

The g values are different from those of the O_2^- species ($g_z = 2.058$, $g_x = g_y = 2.003$) on oxygenated apatite reported earlier [12,13]. Dugas and Rey [13] assumed that O_2^- was located in the channel at $z = c/2$ in which the O–O axis was inclined with respect to the c axis of the apatite. The g_z value lies at those of O_2^- adsorbed on 2+ charged cations by considering the relationship between the variation of g_z and the oxidation state of the metal ion at which O_2^- is adsorbed [14]. When the relationship was applied to the g_z value of the O_2^- species in
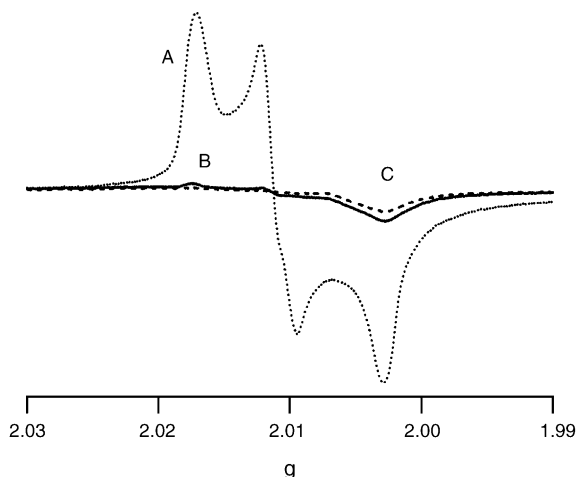

Fig. 1. ESR spectra of O_2^- and the subsequent reaction with C_3H_6. (A) O_2^-; (B) after the reaction with C_3H_6 for 3 min; (C) for 8 min.
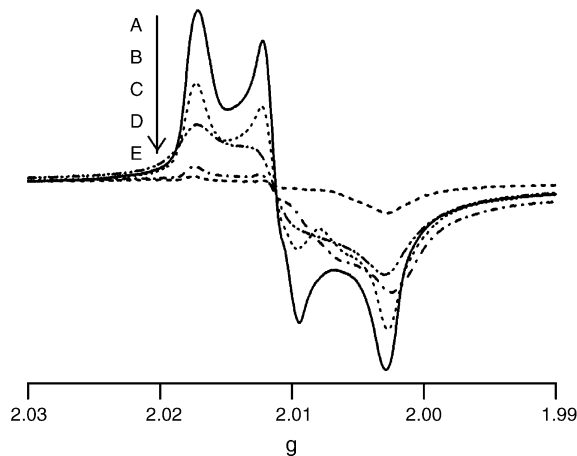

Fig. 2. The ESR spectra of the O_2^- species reacted with C_3H_6, CH_4, H_2 and C_6H_6 for 3 min. (A) O_2^-; (B) C_6H_6; (C) H_2; (D) CH_4; (E) C_3H_6.

Fig. 1, it should be adsorbed on triangle (Ca_3) as if (Ca_3) is a metal ion with 6+ valence state. The $^{17}O_2^-$ ESR signal on HAP showed equivalence of two oxygen atoms [7]. The g values are very similar to those (2.0169, 2.0091, 2.003) reported by Meguro and Ikeya [15] and also resemble those formed on UV-irradiated HAP [16], but the O_2^- species produced on the thermally heated HAP in this study were less stable than the O_2^- species reported by them [15,16]. The O_2^- species were slowly decayed as described in the previous paper on standing without O_2 in the gas phase and the half of it decayed after 30 h [10]. When evacuation was continued, the decay was accelerated.

When propylene (10 Torr) was reacted with the O_2^- species, the intensity of the O_2^- signal rapidly decreased and the signal completely disappeared after 8 min (Fig. 1C). A similar behavior was observed for ethylene. The decay of O_2^- was slower for methane and hydrogen (Fig. 2). The reactivity of terminal olefins with O_2^- was higher than those of saturated hydrocarbons and hydrogen. The ESR spectra after complete reactions of O_2^- with propylene, gave small signals ($g_\perp = 2.0067$, $g_{||} = 2.0021$) (Figs. 1C and 2E).

3.2. ESR spectra in the reaction between O_2^- and benzene

On the contrary, the reaction of O_2^- with benzene was different from those with aliphatic hydrocarbons and hydrogen (Figs. 3 and 4). The intensity of the O_2^- signal slowly decreased in parallel with the gradual formation of a new signal ($g_\perp = 2.0065$, $g_{||} = 2.002$) (Figs. 3D and 4A). The g parameters of the species are very similar to those of CO^- radical on HAP [17]. The resulting signal decreased by half by heating in vacuo at 473 K for 10 min and disappeared by heating at 573 K for 10 min (Fig. 4B). The subsequent contact with O_2 (1 atm) at room temperature for 3 min gave a signal ($g_1 = 2.0078$, $g_2 = 2.0052$, $g_3 = 2.0022$) and a small signal of O_2^- (Fig. 4C). The former might be CO_3^- species by considering of their g values [18]. Further reaction with O_2 (1 atm) for 5 h gave the O_2^- signal ($g_1 = 2.0017$, $g_2 = 2.0011$, $g_3 = 2.003$) with the intensity by 1/5 of the original one while decreasing the intensity of the newly formed signal about the same quantity. More contact with
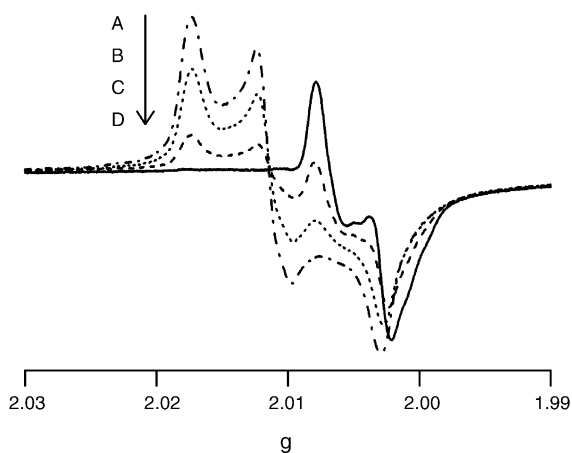
Fig. 3. The ESR spectra in the reaction between O_2^- and benzene. (A) O_2^-; (B) after 3 min; (C) 13 min; (D) 150 min.
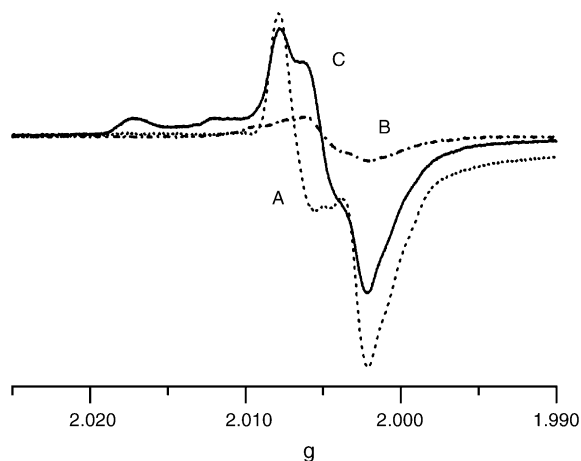

Fig. 4. The ESR spectra in the reaction between O_2^- and benzene. (A) After 150 min; (B) after heating in vacuo at 573 K for 10 min; (C) then on contact with O_2 (1 atm) for 3 min.

O_2 (1 atm) for 1 day resulted in further increase of O_2^- signal intensity by 1/3. The O_2^- must be slowly produced from CO_3^- by an electron transfer.

3.3. The ESR spectral change of the HAP heated at 673–973 K followed by O_2 treatment after the reaction of O_2^- with propylene

After the reaction of O_2^- on HAP with propylene was completed, the HAP was heated at 673 K in vacuo for 1 h and then

treated with O_2 at room temperature, a small and broad signal was observed (Fig. 5a). The HAP was successively heated in vacuo at 773, 873 and 973 K for 1, 1 and 0.5 h, respectively, and treated with O_2 at room temperature in each run. The ESR spectra differed from one another (Fig. 5b–d). Prior to O_2 treatment there was a small and broad signal very similar to the signal obtained by heating at 673 K (Fig. 5a, c-A and d-A). No change of the signal position was observed
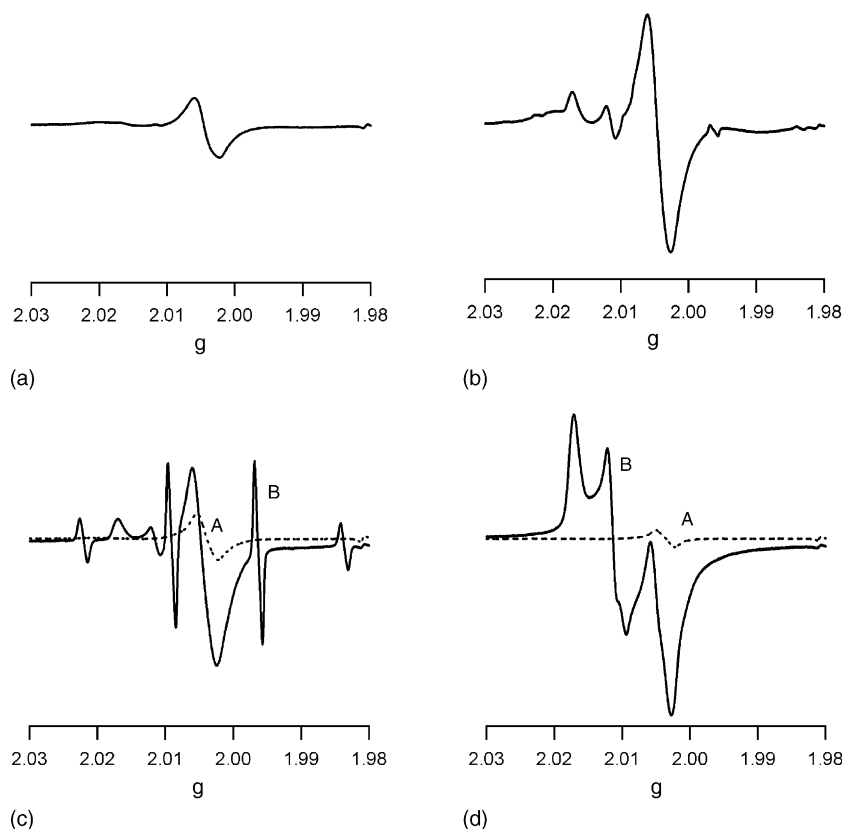

(a)

(b)

(c)

(d)

Fig. 5. The ESR spectra of HAP after heat treatment at 673–973 K and the subsequent reaction with O_2. (a) 673 K; (b) 773 K; (c) 873 K: (A) after heat treatment and (B) after O_2 treatment; (d) 973 K: (A) after heat treatment and (B) after O_2 treatment.
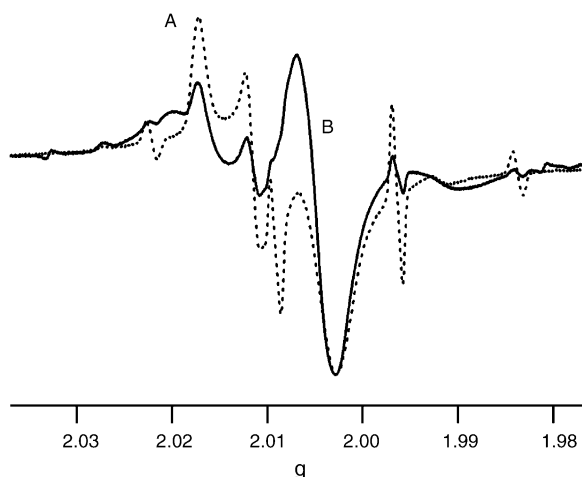
Fig. 6. ESR spectra of HAP after O_2^- was reacted with C_2D_4 and H_2 followed by heating at 823 K for 30 min and treating with O_2. (A) C_2D_4 and (B) H_2.

Fig. 7. The structure of a part of HAP in the neighborhood of OH group.

after O_2 treatment, but its intensity was increased at higher temperatures.

The most striking is that a quartet hyperfine signal ($g = 2.002$, $a = 2.15$ mT) was observed for the HAP with heating at 873 K for 1 h followed by treating with O_2 (Fig. 5c-B). A small such signal was observed in Fig. 5b (heating at 773 K). The quartet lines should be derived from either CH_3 group or three equivalent phosphorus atoms, since the nuclear spins of hydrogen and phosphorus are both 1/2. Prior to heat-treatment, propylene had been reacted with O_2^-. At this moment no quartet signal was observed. It is very doubtful that CH_3 group can be restored once it disappears even if it is formed from the splitting of C_3H_6 in the reaction with O_2^- (Fig. 1C) and subsequently heating at 873 K (Fig. 5c-A). Considering the g value (2.002) three phosphorus atoms should interacted with the unpaired electron on HAP.

Hydrogen was treated with O_2^- on HAP and the HAP was heated at 823 K for 30 min followed by treating with O_2 at room temperature for 2 h. A quartet signal emerged (Fig. 6B) although its intensity was less than that in Fig. 5c-B. Since there was no carbon species in the system, the quartet signal should be attributed to the hyperfine structure of three equivalent phosphorus atoms.

Further evidence was obtained from the reaction with tetradeuterated ethylene. It was reacted with O_2^- followed by heating at 823 K for 30 min and treated with O_2 (1 atm) at room temperature for 90 min. The quartet lines (Fig. 6A) are the same as those shown in Fig. 5c-B, indicating that the quartet lines do not derived from methyl (CD_3) group. The O_2^- species were also observed in Fig. 6A and B.

The O_2^- species were newly produced on MgO which was thermally activated in vacuo and treated with H_2, CO, ethylene or pyridine prior to O_2 adsorption [19–22]. Indovina and Cordischi [20] attributed the electron donor center to a coordinatively unsaturated O_s^{2-} (O_{CUS}^{2-}). We already assumed that O_2^- was produced from the reaction between O_2 and O_{CUS}^{2-} generated by the dehydration of hydroxyl groups situated along the c axis (Fig. 7) [9]. The source for forming the unpaired elec-
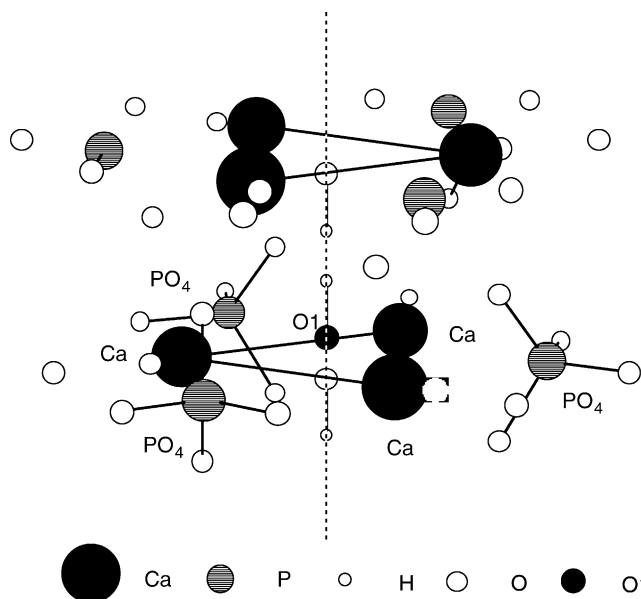
tron interacted with three phosphorus atoms (Fig. 7) is a different type of O_{CUS}^{2-} where higher electron density is donated by the reaction of O_2^- and propylene or hydrogen followed by heat treatment.

The O_{CUS}^{2-} or Fs^+ center reacted with atmospheric oxygen to give O_2^- similar to the cases of MgO [23–25]. There are three equivalent phosphorus atoms from the center of Ca_3 triangle. The small hyperfine constant of 2.15 mT is due to the weak interaction between a newly formed unpaired electron and somewhat remote phosphorus atoms (O1-P = 0.36 nm).

No O_2^- was formed from fluoroapatite heated at 973 K in vacuo for 1 h followed by treating with O_2 (1 atm) for 18 h. It can be concluded that the O_{CUS}^{2-} species derived from hydroxyapatite are responsible for producing reactive O_2^- species.

4. Conclusion

The O_2^- species were generated by heating HAP in vacuo at 973 K followed by treating with oxygen at room temperature. When the O_2^- species were reacted with propylene (or ethylene, hydrogen) followed by heating in vacuo at 873 K for 1 h and treating with oxygen at room temperature, a quartet signal was formed. The quartet signal was derived from the interaction between the newly formed unpaired electron and three equivalent phosphorus atoms a little remote from the center of Ca_3 triangle. The unpaired electron must be formed from a different type of O_{CUS}^{2-} where higher electron density is heightened by the reaction of O_2^- and propylene followed by heat treatment.

Acknowledgement

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