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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.

Keywords: Hydroxyapatite; ESR; Oxygen radical; Oxidation with oxygen

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]:

$$2OH^- \rightarrow O_{CUS}{}^{2-} + \square + H_2O \quad (1)$$

$$O_{CUS}{}^{2-} + O_2 \rightarrow O_2^- + O^- \quad (2)$$

where □ 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, 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.

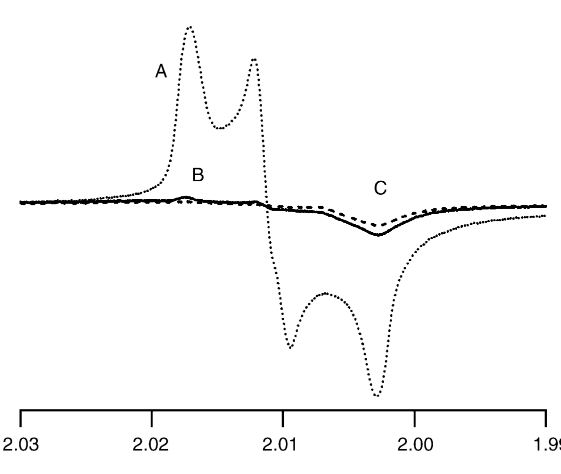

Fig. 1. ESR spectra of O_2^- and the subsequent reaction with C_3H_6. (A) O_2^-; (B) after the reaction with C_3H_6 for 3 min; (C) for 8 min.

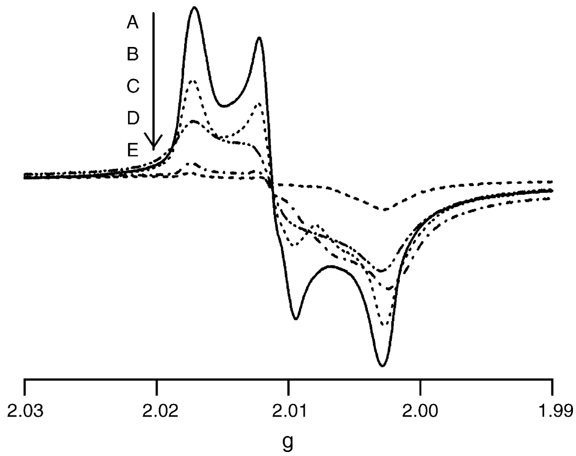

Fig. 2. The ESR spectra of the O_2^- species reacted with C_3H_6, CH_4, H_2 and C_6H_6 for 3 min. (A) O_2^-; (B) C_6H_6; (C) H_2; (D) CH_4; (E) C_3H_6.

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