AN ELECTRON SPIN RESONANCE STUDY OF OXYGEN RADICALS ON HYDROXYAPATITE

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Abstract Oxygen was activated on hydroxyapatite which was previously heated in vacuo above 773K or irradiated with an ultra-high pressure mercury lamp. In the former method O_2^- species gradually formed and slowly decayed. In the latter method two types of O_3^- species were formed and one species rapidly decayed. The different behavior should depend not only on chemical species but on their location.

INTRODUCTION

There have been few reports on which hydroxyapatites were used as catalysts.¹⁻⁴ Matsumura and Moffat have reported that stoichiometric hydroxyapatite revealed different selectivity in partial oxidation of methane with oxygen for non-stoichiometric one.⁴ We have found that oxygen was activated on hydroxyapatite pre-heated above 773K to give oxygen radicals.⁵ It has been assumed that oxygen radicals take key roles in the selective oxidation. Two methods have been undertaken to activate hydroxyapatite: one is heat-treatment and another is light-irradiation.

EXPERIMENTAL

Hydroxyapatite was prepared from $Ca(NO_3)_2 \cdot 4H_2O$ and $(NH_4)_2HPO_4$ according to the general procedure.⁶ The resulting solid was dried at 393K followed by heating at 773K for 3 h. ESR spectra were recorded with a JES-TE-300 spectrometer(X band) at 77K and room temperature. The oxygen radicals were prepared by two methods. The one was that the sample was heated in vacuo at 973K for 2 h followed by treatment with oxygen at room temperature. Another method was that the sample was heated above 373K for 1 h followed by irradiation with an Ushio ultra-high pressure mercury lamp at 77K for 30 min. Oxygen was reacted with irradiated hydroxyapatite above 243K.

RESULTS AND DISCUSSION

Oxygen radicals on heat-treated hydroxyapatite

After hydroxyapatite was heated in vacuo at 973K for two hours, it was treated with oxygen to give oxygen radicals (Fig. 1) which was assigned as O_2^- in the previous paper.⁵ It gradually formed in O_2 (Fig. 2) and decayed without O_2 on standing (Fig. 3) Evacuation caused signal intensity of O_2^- by 1/6.5 after one hour. These results suggest that adsorbed oxygen species might be formed in the following process;

The superoxides were presumed to be formed on the vacancy sites. Slow formation and slow decay of superoxide radicals were caused by slow diffusion of oxygen along OH channels.

Oxygen radicals on UV-irradiated hydroxyapatite

Hydroxyapatite pre-heated above 373K was irradiated with an ultra-high mercury lamp at 77K to give an ESR signal which was assigned as O^- species ($g_{\perp} = 2.0599$, $g_{\parallel} = 2.0023$) (Fig. 4). The DTA analysis showed the desorption of water at around 330K (Fig. 5). Adsorbed water may block sites to be activated by irradiation. The photoactivated species was too unstable to be kept at room temperature. Oxygen

Fig. 3 Decay of ESR O_2^- signal.

Fig. 1 ESR spectrum of O_2^- on hydroxyapatite.

Fig. 2 Formation of ESR O_2^- signal vs time.

Fig. 4 ESR spectra (77K). (A) (a) After irradiation. (b) After warming to r. t. (B) Difference spectrum.

was treated with O^- species to give O_3^- species (dotted line) with three g values ($g_{xx} = 2.002$, $g_{yy} = 2.011$, $g_{zz} = 2.017$)(Fig. 6) similar to those prepared by low ashing.⁷ The g values are very close to those of the O_2^- species shown in Fig. 1. The species was also prepared by the irradiation of hydroxyapatite in O_2 at room temperature. The 300 - 350 nm light was effective.

After hydroxyapatite was heated in O_2 at 673K for 2 h, no oxygen radicals were observed after evacuation at room temperature. However, hydroxyapatite was cooled to room temperature kept in O_2 and was irradiated resulting in forming two types of oxygen radicals(Fig. 6) One is a type of O_3^- species(dotted line), and another is a different type of O_3^- species(solid line) with three g values($g_{xx} = 2.006$, $g_{yy} = 2.009$, $g_{zz} = 2.014$). On standing the former decays faster than the latter. The decay of the former is of the first order(Fig. 6)($k_1 = 8.3 \times 10^{-3} \text{ min}^{-1}$). The O_3^- species(dotted line) were found to react with carbon monoxide, carbon dioxide, hydrogen, ethylene, etc.

The different decay rates between oxygen radicals produced by heat-treatment and

Fig. 5 DTA analysis of hydroxyapatite

Fig. 7 Decay of ESR O_3^- signal.

Fig. 6 ESR spectra of hydroxyapatite irradiated in O_2 at r. t. (B) Difference spectrum.

light irradiation depend not only on chemical species but on their location. The O_3^- species produced by irradiation were formed on the surface or near the inlet of the channel (Fig. 8) where they could easily escape.

Further investigation on the reactivity of oxygen radicals is now in progress.

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Fig. 8 Structure of hydroxyapatite(a, b plane)