



## Original Research Paper

## FTIR studies of adsorption and photocatalytic decomposition under UV irradiation of dimethyl sulfide on calcium hydroxyapatite

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## ABSTRACT

The adsorption and photocatalytic decomposition under UV irradiation of dimethyl sulfide ((CH<sub>3</sub>)<sub>2</sub>S; DMS) on synthetic colloidal calcium hydroxyapatite (Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>; Hap) particles were examined by *in vacuo* IR measurements. The adsorption isotherms of DMS on Hap exhibited the Langmuir type. The saturated adsorbed amount of DMS was increased with increasing the outgassing temperature of Hap, showing a maximum of 2.4 molecules/nm<sup>2</sup> at 250 °C. Similar tendency could be observed for change in area intensity of surface P-OH bands of Hap estimated from *in vacuo* IR measurements against outgassing temperature. By adsorption of DMS, the surface P-OH bands of Hap weakened while the CH bands due to DMS appeared. These results revealed that the DMS was adsorbed on surface P-OH groups of Hap. When the UV light was irradiated to the DMS-adsorbed Hap, the surface P-OH bands revived and the CH bands weakened. This fact strongly indicated the photocatalytic decomposition of DMS took place on surface P-OH groups of Hap, which was thought to be due to the formation of surface P-OH<sup>•</sup> radicals by UV irradiation.

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## 1. Introduction

Calcium hydroxyapatite, Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub> designated as Hap, is a principal component of hard tissues and has been of interest in industry, medical and dental fields. Synthetic Hap finds many applications such as adsorbents for chromatography to separate protein and enzyme, catalysts for dehydration and dehydrogenation of alcohols, methane oxidation, artificial teeth and bones, and so forth [1–6]. Most recently, the Hap powder is received attentions in application for photocatalyst. Wakamura and co-workers have reported that Ti(IV)-doped Hap possesses a photocatalytic activity for decomposition of acetaldehyde and albumin under ultra violet (UV) irradiation [7]. Further, the material shows a high bactericidal effect owing to its higher affinity with proteins than titanium dioxide (TiO<sub>2</sub>) [7,8]. Since then, some researchers examine the structure, property and application of Ti(IV)-doped Hap powder [9–12]. Hu et al. have indicated that the Hap co-doped with Ti(IV) and antibacterial ions (Ag(I), Cu(II) or Zn(II)) possesses the high efficiency for killing the *Escherichia coli* and *Staphylococcus aureus* [9]. Also, Anmin et al. reported that the photocatalytic activity of Ti(IV)-doped Hap is related to its particle size, crystalline

quality, morphology, specific surface area and surface state [10]. Most recently, Huang et al. suggested that the Ti(IV)-substituted Hap has a great potential for use in biomedical applications such as bioactive scaffolds and coating on Ti implants [12]. On the other hand, one of the authors (H. N.) has reported the generation of ·OH and O<sub>2</sub><sup>•−</sup> radicals on Hap after heating at 200 °C in air and UV irradiation and indicated the photocatalytic decomposition of dimethyl sulfide ((CH<sub>3</sub>)<sub>2</sub>S; DMS) and methyl mercaptan (CH<sub>3</sub>SH) over Hap [13–18]. Although, interaction between DMS and Hap surface is not fully clarified. The aforementioned functions of Hap relate to the various surface properties of Hap, e.g., surface functional groups, acidity and basicity, surface charge, hydrophilicity, and porosity. It has been found that the surface of synthetic Hap particles possesses ca. 2.6 groups/nm<sup>2</sup> of P-OH groups acting as the adsorption sites for CO<sub>2</sub>, CH<sub>3</sub>OH, H<sub>2</sub>O, *n*-butylamine and acetic acid [19–22]. Therefore, the surface P-OH groups seem to be important role for adsorption and photocatalytic decomposition of DMS.

The aim of this study was to clarify the mechanisms of adsorption of DMS on Hap surface and photocatalytic decomposition of DMS under UV irradiation. Therefore, we examined the adsorption of DMS on synthetic colloidal Hap particles and photocatalytic decomposition of DMS under UV irradiation by means of *in vacuo* IR measurements. The adsorption site of DMS on the surface of

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