HAp/TiO2 heterojunction catalyst towards low-temperature thermal oxidation of VOC

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Keywords: volatile organic compounds (VOC), thermal catalytic oxidation, hydroxyapatite (HAp), composite, heterojunction, titanium dioxide (TiO₂)

Abstract
Ceramic catalyst without precious metals and rare-earth elements is a promising technology for removing volatile organic compounds (VOC) produced in the manufacturing process to feasibly solve worldwide health and environmental problems. We first investigate the influence of hydroxyapatite (HAp)/TiO₂ heterojunction formation on the temperature dependence of VOC catalytic performance. The comprehensive evaluation by XRD, FT-IR, UV–vis, and in situ ESR clarifies that the anisotropic crystal distortion along the c-axis of HAp lattice is caused by hydrolysis and hetero-condensation of TiO₂ precursor accompanying with the defective structure in HAp. The structural modified HAp (m–HAp) provides the notable alteration of optical bandgap with the visible-light coloration and the preferential generation of oxygen radicals. Furthermore, we propose a new model that the m–HAp/TiO₂ heterojunction should be a possible main factor affecting the more than twice higher catalytic performance in thermal oxidation of ethyl acetate at a lower temperature, as typically shown in HAp-T1.

1. Introduction

Volatile organic compounds (VOC) are a type of pollutants produced in the manufacturing process using organic solvent for coating and adhesion, putting human beings at risk of various diseases [1–3] in addition to the generation of harmful substances responsible for the worldwide environmental issues [4–6], such as photochemical oxidant and particulate matter (PM). VOC catalytic oxidation using non-noble metals (Pt, Pd, Au, Ag, etc.) has been extensively investigated owing to their excellent performance. However, in addition to cost issues and ease of poisoning [7], precise controlling in morphology, particle size, and dispersibility of metal nanoparticle catalysts on support materials such as Al₂O₃, SiO₂ and zeolite are necessary to maximize catalytic activity [8–10]. Moreover, small and medium-scale facilities for VOC treatment suffer from high running costs and difficulty recycling, usually utilizing a catalytic combustion method with precious metal nanoparticles. In recent years, metal oxide catalysts, including rare-earth metal or transition metal elements, have been reported as cheaper alternatives to noble metals [7]. As examples of metal oxide catalysts, CeO₂ incorporated with Mn ions as Mn–Ce–O catalytic system is reported to efficiently oxidize ethyl acetate and toluene [11]. Highly dispersed CuCe₅Zr₁−xO₄ (x ≤ 0.15) species on ZSM-5 support facilitate the complete conversion of ethyl acetate to CO₂ due to excellent reducibility [12]. In addition, LaMO₁₋ₓMₓ (M = Co, Mn) perovskite with La partially substituted by Sr can reduce lower temperature oxidation of ethyl acetate [13]. However, the imperative requirement in the precise adjustment of chemical composition is the technical drawback.

Recently, our group has proposed a novel oxidation catalysis strategy using a thermal ceramic catalyst based on Ca type hydroxyapatite (HAp; Ca₁₀(PO₄)₆(OH)₂) without precious metals and rare-earth elements for highly efficient removal of VOC [14, 15]. HAp, as a promising earth-abundant and low-cost material with biological
Table 1. Experimental recipe of HAp/TiO2 composite catalyst.

| Sample No. | Hap (g) | TBOT (ml) | \( \varepsilon W_{\text{TiO}_2} \) (wt%) |
|------------|---------|-----------|-----------------------------|
| HAp        | 4.67    | 0         | 0                           |
| HAp-T1     | 4.67    | 5.0       | 3.25                        |
| HAp-T2     | 0.467   | 5.0       | 25.16                       |
| HAp-T3     | 0.156   | 5.0       | 50.16                       |
| TiO2       | 0       | 5.0       | 100.00                      |

2. Experimental procedures

2.1. Synthesis of HAp/TiO2 composite catalyst

A commercial HAp powder with an average particle size of 15 \( \mu \text{m} \) (Taihei Chemical Industrial Co., Ltd, Spherical-HAp; 3Ca(OH)2•Ca(PO4)2) was used as a raw material. The reagents such as titanium tetrabutoxide (TBOT; Ti(OC4H9)4), 1-butanol (C4H9OH), and acetic acid (CH3COOH) were purchased from FUJIFILM Wako Pure Chemical Corporation. For selective coating of TiO2 on the HAp particle surface, the hydrolysis/condensation rate in the sol-gel reaction of TBOT was carefully controlled by the use of acetic acid as a chelating agent for metal alkoxide [21, 22] and the two-step dropping water technique [23, 24]. Firstly, a certain amount of HAp powder was added in 13.2 ml of 1-butanol solution. Following stirring/sonification at R.T. for 15 min, the solution was mixed with TBOT (5.0 ml), 1-butanol (6.7 ml), and acetic acid (1.2 ml). As the next step, 0.13 ml of distilled water was added to this solution with stirring for 30 min at R.T. Finally, the solution with additional distilled water (0.26 ml) was stirred again for 30 min at 50 °C. The precipitated gel-like solids were obtained by centrifugation and washing with ethanol and then calcinated at 550 °C for 3 h for crystallization, following drying at 130 °C for 1 h. The detailed information for the loading amount of HAp powder and sample labels is shown in table 1. Here, a converted weight fraction is defined as follows:

\[
\text{Coverted weight of TiO}_2 (\varepsilon W_{\text{TiO}_2}) = \frac{M_{\text{TiO}_2} \times c_{\text{TBOT}} \times m_{\text{Ti}}}{M_{\text{TBOT}}} \\
\text{Coverted wt\% of TiO}_2 (\varepsilon W_{\text{TiO}_2}) = \frac{c_{W_{\text{TiO}_2}}}{c_{W_{\text{TiO}_2}} + W_{\text{HAp}}} \times 100
\]

where, \( M_{\text{TiO}_2} \) and \( M_{\text{TBOT}} \) is molar mass of TiO2 (= 79.987 g mol\(^{-1}\)) and TBOT (= 340.32 g mol\(^{-1}\)) respectively, \( c_{\text{TBOT}} \) is concentration of TBOT (mol), \( m_{\text{Ti}} \) is atomic mass of Ti (= 47.867 g mol\(^{-1}\)), \( W_{\text{HAp}} \) is weight of HAp (g).

2.2. Characterization methods

The crystal structure of HAp based composite was evaluated by x-ray diffraction (XRD) pattern (UltimaIV, Rigaku) with CuK\(_{\alpha}\) radiation. The reference intensity ratio (RIR) was used for quantitative analysis by powder diffraction [25]. The particle morphology and the distribution of elements on composite were analyzed by field emission scanning electron microscopy (FE-SEM) equipped with an EDS analyzer (JSM-7600F, JEOL). The Brunner–Emmett–Teller specific surface area (SSA\(_{\text{BET}}\)) was evaluated from N\(_2\) adsorption isotherms on a high-precision gas adsorption measurement instrument (BELSORP-mini2, Microtrac BEL, Japan) at 77 K. The measurement of Fourier transform infrared spectra were conducted by FT-IR spectrometer (FT-IR 6600,
The optical properties were investigated by UV–vis spectrophotometry (V-7100, Jasco). Optical bandgap ($E_g$) was determined by applying a modified Kubelka-Munk function as follows:

$$n^2 = -\frac{F(R) \times h\nu}{R}$$

where $R$ is the reflectance, $h\nu$ is the photon energy. Here, the value $n = 2$ was used since HAp has the indirect bandgap [26]. The evaluation of thermal-induced active oxygen radicals on the HAp surface was confirmed by electron spin resonance (ESR) spectra recorded with a JEOL JES-FA200 spectrometer equipped with an in situ heating system in atmospheric conditions. Mn$^{2+}$ was used as an internal standard.

2.3. Evaluation of catalytic performance in the oxidative reaction of VOC gas

The experimental setup was referenced in [27]. The flow reaction system is shown in figure 1. Gaseous volatile organic compounds (ethyl acetate ($C_4H_8O_2$), 100 ppm)/$N_2$ and air were mixed in a 1:1 ratio before feeding to the reaction vessel. The flow rate of mixed gas was controlled at 0.125 l min$^{-1}$ by a flow meter (FCC-3000P-G1,
KOFLOC, and the heating temperature was in the range of 100 °C–400 °C by tube furnace (KTF030N1, KOYO thermo systems co., Ltd, JAPAN). As gas generation evaluation in VOC oxidation catalysis, the concentration of CO2 and CO was detected by using CO monitor (UM-300, KOMYO RIKAGAKU KOGYO K.K.) and CO2 infrared absorption monitor (RI-215D, RIKEN KEIKI co., Ltd). Before the catalytic evaluation, no conversion from ethyl acetate to CO or CO2 was confirmed in the range of 0 °C–500 °C due to self-oxidation (Figure is not shown).

3. Results and discussion

3.1. Structure of HAp catalyst composited with TiO2

Figure 2(a) shows XRD patterns of the pristine HAp and the synthesized composites. The new diffraction peaks are identified as anatase TiO2 (COD card No. 9015929). The intense peaks of anatase are observed with the increase of c'WTiO2 in the synthesis, while the peak intensity of HAp gradually decreases. Figure 2(b) displays the nonlinear increase in the reference intensity ratio (RIR) value of anatase TiO2, plotted as a function of c'WTiO2, indicating an increase of wt% of anatase in the whole crystal phase of composites. Moreover, the significant change in FWHM of the (002) plane of HAp crystal is observed in the composite specimen with large c'WTiO2 to compare with the (300) plane (figure 2(c)). Generally, PO4 and OH sites are highly arranged along c-plane rather than a-plane. The alkoxides hydrolysis is catalyzed by the presence of ceramics particles with the OH group, leading to a fast hetero-condensation reaction [22, 28]. Moreover, it is known that OH-PO4 can work as an active
site for generating TiO₂ during hydrolysis of metal-alkoxide precursors. Therefore, it is considered that the deficient structure prefers to be anisotropically formed in not a-plane but c-plane of HAp, and the excess amount of TiO₂ precursor results in the destruction of HAp crystal. Further evidence for the strong interaction between two materials can be confirmed in the lattice structure of anatase TiO₂. Figure 3 shows the values of lattice parameters (a and c) and unit-cell volume of anatase TiO₂ compositied in HAp catalyst. The anisotropic expansion along the c-axis is confirmed by increasing $c'_{\text{WTiO}_2}$ compared with the change along the a-axis, increasing unit-cell volume. Such lattice expansion, especially along the c-axis, is often observed in reduced TiO₂ because the nearest-neighbor Ti atoms move away from the vacancy due to the absence of electrostatic attraction. Thus, oxygen-deficient TiO₂ would be formed in the composites through the synthesis with large $c'_{\text{WTiO}_2}$, indicating strong interaction in the interface between two materials through hydrolysis and hetero-condensation on the HAp surface distortion of HAp lattice.

Figure 4 shows the N₂ adsorption/desorption isotherm and the summary of BET-specific surface area (SSA_BET) of the pristine HAp and the synthesized composite particles.

Figure 4. (a) N₂ adsorption/desorption isotherm. (b) BET specific surface area (SSA_BET) of the pristine HAp and the synthesized composite particles.

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$c'W_{TiO2}$. As shown in the distribution of elements (Ca, P, O, and Ti) evaluated by SEM-EDS mapping (figure 5), Ti elements distribute uniformly in the composite particles (HAp-T1).

The chemical structure of HAp was not significantly changed after forming a composite structure in FT-IR spectra (figure 6). The peaks at 1645 and 3470 cm$^{-1}$ are assigned as the vibration from H$_2$O bending and H$_2$O stretching. The specific bands of HAp as PO$_4$ bands ($\nu_3$: 1095 and 1045 cm$^{-1}$, $\nu_4$: 965 cm$^{-1}$, $\nu_2$: 635, 600 and 565 cm$^{-1}$, $\nu_2$: 460 cm$^{-1}$) and OH$^-$ stretching (3565 cm$^{-1}$) [33, 34] are also observed. In terms of the chemical structure from HAp, there are no notable changes in the composites to compare with the pristine HAp. The wide broadened band at 400–1000 cm$^{-1}$ can be assigned to Ti–O–Ti vibrations [35] since it appears a large amount of TiO$_2$ precursor was added.

The pristine HAp shows the poor light-absorbing capacity in the entire region of UV–vis, as shown in figure 7(a), while the significant enhancement in UV and blue light region is confirmed in the synthesized composite even with small $c'W_{TiO2}$ (HAp-T1). There are two possible reasons for such coloration; involved by (1) oxygen vacancies or deficient structure in a PO$_4$ group/OH group [36], (2) substitution of Ti element into Ca site in HAp crystal [37]. Moreover, as the characterization of the optical bandgap of the pristine and synthesized TiO$_2$, the bandgap (3.14 eV) is slightly lower than pure anatase TiO$_2$ (3.2 eV) due to oxygen vacancies on the TiO$_2$ surface (not shown). In our case, oxygen-deficient TiO$_2$ would form because of the synthesis with a small amount of H$_2$O for hydrolysis in sol-gel reaction if there is less influence from the hetero-condensation with the HAp surface.

3.2. ESR analysis
ESR spectra are strongly affected by the chemical structure of HAp synthesized by different synthesis methods [41]. For example, in the ESR spectra of the pristine HAp, the signal with $g = 2.0028$ gradually appears by raising...
the temperature from 300 °C to 400 °C (figures 8(a)–(b)). This signal is assigned with oxygen radical [42], observed by the deformation of the P-OH group from the HAp surface. In contrast, HAp-T1 shows an intense signal even at 300 °C. Besides, there are no signals attributed by trapped electrons (g = 1.988) and crystalline defects (g = 1.999) from Ti-HAp [43] as well as by oxygen radical in TiO2 (g = 2.003) [44]. Moreover, the typical signal caused by anatase Ti3+ defects (g = 1.992) [45] does not appear in our synthesized HAp/TiO2 composites and the synthesized TiO2 particles without HAp (figure 8(c)). This case would be directly related to the low-temperature generation of oxygen radicals by the anisotropic distortion of HAp lattice stabilized in the composite interface. Moreover, the amount of TiO2 in the composite is also a critical factor that preferentially causes the loss in the probability of radical generation because the pristine HAp hardly retains the crystal structure due to strong destruction. From these results, the change in optical bandgap observed from UV–vis spectra (figure 6) should be described by not Ca site defects on Ti-doped HAp but the structural defects in the OH-PO4 site of HAp.

3.3. VOC catalytic performance

Figure 9 summarized the catalytic performance, which is evaluated by the conversion rate of VOC (ethyl acetate) into CO or CO2 plotted as a function of the reaction temperature (R.T.–400 °C). There is the notable difference that the CO/CO2 conversion capacity is twice higher in the HAp-based composite catalyst with the small c-W_TiO2 (HAp-T1) than the pristine HAp catalyst at a lower temperature region (300 °C), despite the deterioration of catalytic activity at higher temperature region (400 °C). On the contrary, a significant deterioration is also observed in the composite catalyst with excess anatase TiO2 (HAp-T3). The synthesized anatase TiO2 through sol-gel reaction exhibits the thermal activation in VOC decomposition; however, catalytic
performance is still lower than HAp catalyst. Although the value of $SSA_{\text{BET}}$ of catalyst is regarded as one of the factors on an enhancement of VOC decomposition performance \cite{46}, the improvement of catalytic performance in HAp-T1 cannot be described only by $SSA_{\text{BET}}$, and also being not critically affected by the amount of anatase TiO$_2$ in composite (figure 10). This fact certainly indicates the synergistic effects of composite catalysts, which enhance the performance at low temperatures by building up the specific heterostructure between two materials. There is a strong correspondence between the VOC catalytic activity at low temperature and the signal intensity from the generated radical species in ESR spectra.

### 3.4. Possible mechanism of enhancement of catalytic performance at low temperature in HAp/TiO$_2$ heterojunction

As the well-established mechanism of catalytic activity in photo-activated catalyst \cite{47}, the formation of oxygen radicals is a critical intermediate state through the reaction that the excited carrier (electron and hole) by external energy is scavenged by surface oxygen. A similar mechanism of radical generation has been proposed in the case

![Figure 7](image-url). (a) UV–vis spectra. (b) tauc-plot.
Moreover, our group previously reported that the origin of ·O$_2^-$ radical species as an accelerator to degrade VOC gas during heating is the electron transfer from the locally disordered structure through the desorption of OH group in HAp crystal [14, 15]. Here, we consider that HAp/TiO$_2$ heterojunction...
Figure 9. Evaluation of catalytic performance in VOC (ethyl acetate) oxidation reaction in the range of R.T. $-400^\circ$C.

Figure 10. (a) RIR of anatase TiO$_2$ versus CO/CO$_2$ conversion rate, (b) SSA$_{BET}$ versus CO/CO$_2$ conversion rate.
in the interface between two materials plays a vital role in efficiently transferring thermal-induced electrons, which directly relates to enhancing catalytic performance at low temperatures.

Figure 11 is the schematic illustration of the band structure with/without the modified-HAp (m-HAp)/TiO2 heterojunction. The thermally-induced carriers (electrons and holes) on TiO2 catalysts are also known to involve the oxidative reaction \[48, 49\]. Therefore, the HAp/TiO2 heterojunction should help reduce recombination of thermal-induced electrons since the localized energy state by OH defects in HAp would have more positive potential than conduction band minimum (CBM) of anatase TiO2. On the other hand, the defects such as Ti\(^{3+}\) and oxygen vacancies on defective TiO2 (TiO\(_x\)) form the impurity level localized at 0.75–1.18 eV below CBM \[50\]. The impurity level should have more negative potentials than O\(_2^-\)/O\(_2^{2-}\) (−0.33 V, V versus NHE) \[51\], then the generation of active ·O\(_2^-\) radicals is prevented due to poor electron transfer efficiency to react with O\(_2\). One reason that no signal attributed to oxygen radical from TiO2 is observed in the ESR spectra of HAp catalyst compositive with anatase TiO2. In the case of the composite catalyst with a large wt\% of TiO2, the catalytic performance in the oxidative decomposition of ethyl acetate deteriorates due to the preferential generation of TiOx and the substantial destruction of HAp lattice as an inert structure for the oxidative reaction of VOC gas.

4. Conclusions

We firstly investigate the influence of modified-HAp/TiO2 heterojunction on the temperature dependence of catalytic performance in VOC oxidative decomposition by HAp based thermal ceramic catalyst without precious and rare-earth metal nanoparticles. The structural-modified HAp catalyst compositive with anatase TiO2 is synthesized through the conventional method using a sol-gel reaction of titanium alkoxide. The comprehensive evaluation by XRD, FT-IR, UV–vis, and \textit{in situ} ESR clarified that the anisotropic distortion along the c-axis of HAp lattice causes the oxygen vacancies in PO\(_4\) sites and the defective structure of OH group through hydrolysis and hetero-condensation of TiO2 precursor with HAp surface. Furthermore, it would lead to
the notable alteration of optical bandgap with the visible-light coloration from >6.0 eV to 3.61–3.86 eV and the low-temperature generation of oxygen radicals caused by the defective structure HAp lattice. Based on the results, we propose a possible mechanism that the modified-HAp/TiO2 heterojunction in the composite catalyst would be the main factor to involve the more twice higher enhancement for the efficiency in the oxidative reaction of ethyl acetate gas at a lower temperature (300 °C) with the appropriate weight fraction of TiO2 (typically shown in HAp-Ti1). Therefore, these results provide a guideline for a material design in structure and interface towards creating further efficient VOC oxidation catalysis at low temperatures.

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