

## Short communication

## In situ photoacoustic FTIR studies on photocatalytic oxidation of 2-propanol over titanium(IV) oxide

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## ABSTRACT

Adsorption and photocatalytic reaction of 2-propanol over titanium(IV) oxide (TiO<sub>2</sub>) were studied by Fourier transform infrared spectroscopy (FTIR) using a photoacoustic (PA) technique. At first, the validity of the FTIR system using a home-made PA cell was confirmed by comparison with conventional transmission FTIR. The spectrum of TiO<sub>2</sub> with 2-propanol showed different propoxy peaks from those of gaseous 2-propanol as a result of chemisorption on TiO<sub>2</sub>. Finally, in situ FTIR observation of the photocatalytic oxidation of 2-propanol was carried out. Under ultraviolet irradiation, PA spectra changed due to complete oxidation of 2-propanol through acetone as an intermediate.

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## 1. Introduction

Environmental remediation using a semiconductor photocatalyst such as titanium(IV) oxide (TiO<sub>2</sub>) particles has attracted much attention because photocatalytic materials enable the removal of hazardous materials in an environmentally friendly way by utilization of light energy in a redox reaction [1,2]. Various photocatalytic evaluation methods for practical applications, e.g. water remediation, air purification and self-cleaning effect, have been proposed and the evaluation method for the photocatalytic performance has been standardized [3]. The removal of volatile organic compounds (VOC) is one of the conventional evaluation methods. Usually, gaseous products that are generated by photocatalytic oxidation of VOC are evaluated by analysis of a certain volume of sampling gas with gas chromatography, and carbon dioxide (CO<sub>2</sub>), which is the final product of oxidation of an organic compound, is conventionally estimated as photocatalytic activity in most cases [3]. However, some intermediate products that have a high boiling point and strong absorption on the photocatalyst surface are not detected by this method. In such cases, ex situ qualitative analysis should be carried out after the reaction [4,5].

Fourier transform infrared spectroscopy (FTIR) is a possible method for observation of compounds adsorbed on the photocatalyst surface,

and in-situ FTIR measurements have been studied [6–9]. For FTIR measurement of semiconductor particles, a special set-up has often been used to estimate photoabsorption because strongly scattering materials cannot be accurately evaluated by conventional transmission. Recently, the attenuated total reflection (ATR) technique has been widely used for FTIR measurements to observe a catalytic interface during illumination [10–13]. Although the ATR technique is suitable for investigating solid–liquid interfaces of particle, compared to the diffuse reflectance (DR) technique, little information on the gas phase over a catalyst is obtained. Moreover, particle size must be below the penetration depth of light because the sample is photoirradiated from the opposite side to the solid–liquid interface that is observed by the ATR technique.

Photoacoustic (PA) technique is one of possible methods for in situ observation of a photocatalytic reaction over semiconductor nanoparticles without any pretreatment in the same way as a normal photocatalytic reaction, and PA technique is applicable to even opaque and strongly scattering solid materials because photoabsorption is detected by photothermal waves [14,15]. Photoacoustic Fourier transform infrared spectroscopy (FTIR-PAS) has been studied for photochemical reaction [16], solid-gas reaction [17] and comparison with DRS and ATR [18], but there have been no studies on in situ observation of a photocatalytic reaction over semiconductor particle. We have used PAS for in situ observation of a photocatalytic reaction, and trivalent titanium species [19,20] and heat of an exothermic reaction [21] were detected with photocatalytic reaction over TiO<sub>2</sub> powder. In the present study, we established an FTIR-PAS system using a home-made PA cell

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for in situ observation, and we compared the results with those obtained by conventional transmission. We also detected IR adsorption attributable to 2-propanol over  $\text{TiO}_2$  powder using the PA technique. Finally, in situ FTIR observation of photocatalytic 2-propanol oxidation was studied, which is the first study for the FTIR measurement conducted in the same way as a normal photocatalytic reaction.

## 2. Experimental

### 2.1. FTIR-PAS measurements

For FTIR-PAS measurements, a home-made PA cell composed of a duralumin body with an inner volume of ca. 0.2 mL ( $8\text{ mm}\Phi \times 4\text{ mmH}$ ), a calcium fluoride ( $\text{CaF}_2$ ) window and two valves for gas exchange was used. Digital photograph of a home-made PA cell is shown in supplementary Fig. S1. An FTIR spectrometer (Nicolet, iS 10) was used as interference IR sources. The digital PA signal acquired by a digital MEMS microphone (Invensense, ADMP441) buried in the cell was recorded by using a PC equipped with digital I/O devices. The interferogram acquired by analog conversion of the digital PA signal was Fourier-transformed with the Happ-Genzel window function, and the PA spectra were obtained by normalizing with carbon black powder as a reference to compensate wavenumber-dependent light intensity.

### 2.2. Adsorption of 2-propanol on $\text{TiO}_2$ powder

Commercially available  $\text{TiO}_2$  powder supplied by Showa Denko (Super-Titania F6 A) was used without any pretreatment and placed in the PA cell. The atmosphere was controlled by a flow of oxygen with or without 2-propanol vapor, and FTIR measurements were carried out after shutting off the valves, i.e., in a closed system at room temperature.

### 2.3. Photocatalytic oxidation of 2-propanol over a $\text{TiO}_2$ film

$\text{TiO}_2$  powder (Super-Titania F6 A) was uniformly spread on a glass plate ( $6.0\text{ mm}\Phi \times 0.09\text{ mm}$ ) by the squeegee method, and the plate was placed in the PA cell. Oxygen containing gaseous 2-propanol ( $0.66\text{ mmol L}^{-1}$ ) was injected into the cell using a gastight syringe, and measurements were carried out in the closed system at room temperature. Ultraviolet (UV) irradiation was performed through a window on the top of the cell using a light-emitting diode (Nichia NCSU033B, emitting around  $365\text{ nm}$ ,  $10.5\text{ mW cm}^{-2}$ ) after 2-propanol had reached an adsorption equilibrium. The concentrations of 2-propanol, acetone and  $\text{CO}_2$  were estimated by FTIR measurements using the PA technique.

## 3. Results and discussion

### 3.1. Confirmation of the validity of FTIR-PAS measurements

Fig. S2 shows a power spectrum of the light source obtained by conventional FTIR measurement and a non-normalized PA spectrum of carbon black powder. It is known that PA intensity is in principle proportional to the absorption, but PA intensity is saturated in the range of strong absorption and depends only on intensity of light source, as seen in PA spectrum of carbon black powder [14]. Therefore, it is reasonable that the spectra were in agreement, though a slight difference was observed in the lower wavenumber region ( $<1200\text{ cm}^{-1}$ ) due to transmittance loss of the  $\text{CaF}_2$  window of the PA cell.

Fig. 1 shows FTIR spectra of polystyrene standard obtained by transmission and PA spectrum of polystyrene foam. Although the peak intensity ratios were slightly different, the peak positions were the same. These results are reasonable since polystyrene foam is a mixture of polystyrene and gas. Moreover, the results showed that the PA technique can be used to evaluate an opaque material such as polystyrene foam without pretreatment.

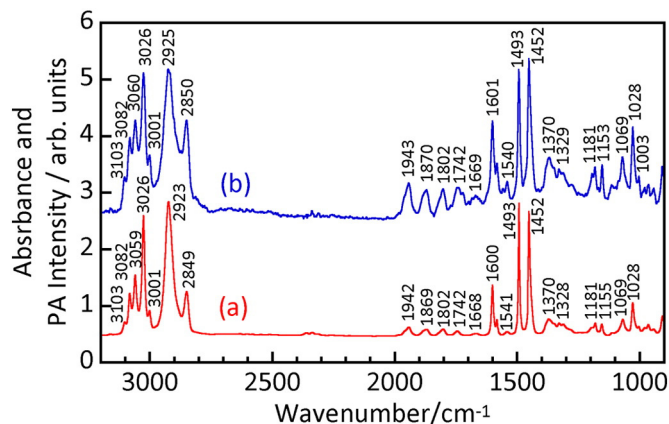


Fig. 1. (a) FTIR spectra of polystyrene standard obtained by transmission and (b) PA spectrum of polystyrene foam.

### 3.2. PA spectra of $\text{TiO}_2$ powder adsorbed with 2-propanol

Figs. 2 and S3 show PA spectra of  $\text{TiO}_2$  powder in an oxygen atmosphere, gaseous 2-propanol and  $\text{TiO}_2$  powder in an oxygen atmosphere containing 2-propanol. Characteristic peaks at  $2981$ ,  $1461$ ,  $1381$ ,  $1251$ ,  $1154$  and  $1072\text{ cm}^{-1}$  attributed to  $\nu(\text{CH})$ ,  $\delta_{\text{as}}(\text{CH}_3)$ ,  $\delta_{\text{s}}(\text{CH}_3)$ ,  $\delta(\text{OH})$ ,  $\nu(\text{CO})$  and  $\nu(\text{CC})$  of 2-propanol [9,22] were observed in the PA spectrum of  $\text{TiO}_2$  in an atmosphere containing 2-propanol, and the spectrum was slightly different from that of gaseous 2-propanol. Xu et al. observed peaks at  $1362$ ,  $1166$  and  $1124\text{ cm}^{-1}$  attributed to  $\nu(\text{CO})$ ,  $\nu_{\text{as}}(\text{CH}_3)$  and  $\nu_{\text{s}}(\text{CH}_3)$  of the chemisorbed 2-propoxide species, respectively [7]. Actually, peaks in this region of the difference spectrum (Fig. 2d) were observed in the present study. A small peak in the range of  $3100\text{--}3500\text{ cm}^{-1}$  was also observed, and it is presumably attributed to  $\nu(\text{O-H})$  of water formed during the reaction process of 2-propanol with the OH group on the  $\text{TiO}_2$  surface [7,9]. These results indicate that not only gaseous 2-propanol but also adsorbed 2-propanol on  $\text{TiO}_2$  was detected by the PA technique.

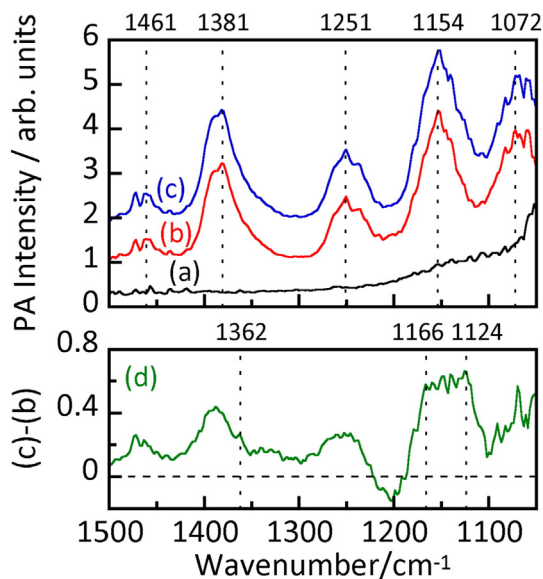


Fig. 2. PA spectra of (a)  $\text{TiO}_2$  powder in an oxygen atmosphere, (b) gaseous 2-propanol and (c)  $\text{TiO}_2$  powder in an oxygen atmosphere containing 2-propanol, and (d) difference spectra of (c)-(b).

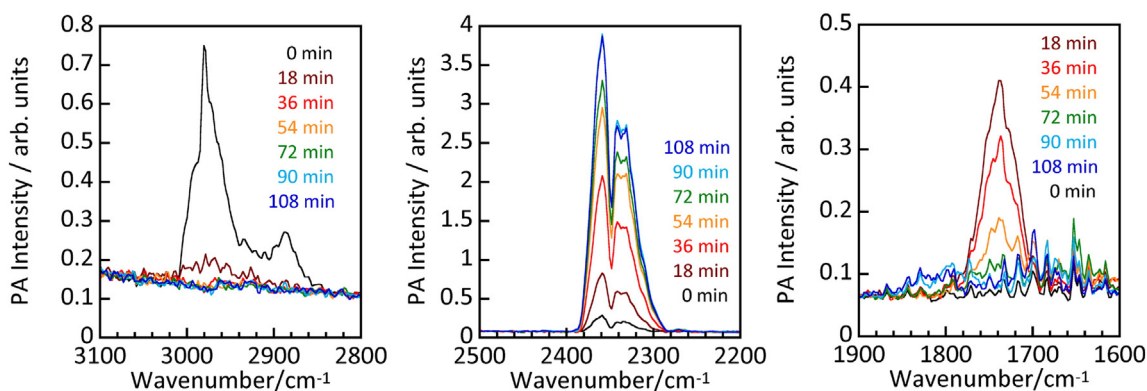


Fig. 3. PA spectra of a TiO<sub>2</sub> film in an oxygen atmosphere containing 0.66 mmol L<sup>−1</sup> of 2-propanol under UV irradiation.

### 3.3. Photocatalytic oxidation of 2-propanol over a TiO<sub>2</sub> film

In situ observation of photocatalytic oxidation of 2-propanol over a TiO<sub>2</sub> film was carried out using FTIR-PAS. Fig. 3 shows PA spectra of TiO<sub>2</sub> in an oxygen atmosphere containing 0.66 mmol L<sup>−1</sup> of 2-propanol. Characteristic peaks at 2981, 1388, 1250, 1154 and 1070 cm<sup>−1</sup> attributed to 2-propanol were observed in the PA spectrum at 0 min. Under UV irradiation, intensities of these peaks decreased, while peaks at 1737, 1365 and 1216 cm<sup>−1</sup> attributed to  $\nu(\text{CO})$ ,  $\delta_s(\text{CH}_3)$  and  $\nu(\text{CC})$  of acetone [9] appeared and they disappeared with longer photoirradiation. It is well known that acetone is generated as an intermediate product during photocatalytic oxidation of 2-propanol [23,24]. Therefore, these peaks are attributed to acetone generated by oxidation of acetone, as a result of 2-propanol oxidation. The assignment of these peaks is reasonable according to results shown in Section 3.2 and literature values [7,9]. On the other hand, the peak in the range of 2300–2380 cm<sup>−1</sup>, which is attributed to CO<sub>2</sub>, monotonically increased with increase in irradiation time.

Fig. 4 shows the time courses of concentrations of 2-propanol, acetone and CO<sub>2</sub> in the PA cell with photocatalytic reaction over TiO<sub>2</sub>. The concentrations of 2-propanol, acetone and CO<sub>2</sub> were determined by the peak intensities at 2981, 1737 and 2359 cm<sup>−1</sup>, respectively, of the PA spectra and standard curve for semi-quantitative determination. The time course showed a representative kinetic curve for the consecutive reaction. With longer photoirradiation, CO<sub>2</sub> reached saturation at 2.0 mmol L<sup>−1</sup>, suggesting total decomposition of 2-propanol to CO<sub>2</sub>. These results indicate that normal photocatalytic oxidation of 2-propanol proceeds in the PA cell as observed in a photocatalytic reactor, and this technique can therefore be applied to observation of a reaction

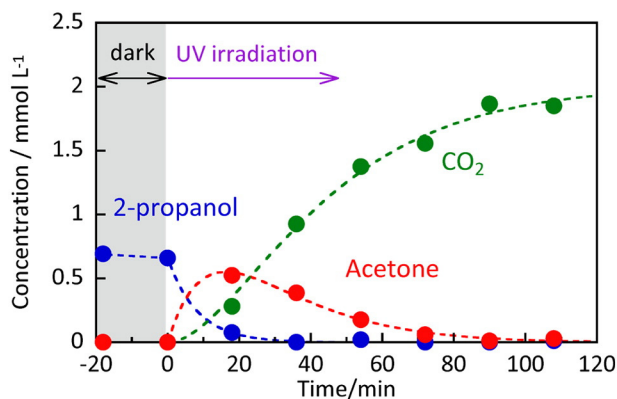


Fig. 4. Time courses of concentrations of 2-propanol, acetone and CO<sub>2</sub> in the PA cell under photocatalytic reaction over a TiO<sub>2</sub> film.

in a micro reactor because gas sampling is not required for product analysis.

### 4. Conclusion

We have shown the validity of FTIR-PAS measurement and applied it to observation of a photocatalytic reaction. FTIR-PAS measurements of TiO<sub>2</sub> powder showed that PA spectra were reflected by not only gaseous 2-propanol but also 2-propanol adsorbed on TiO<sub>2</sub>. FTIR-PAS measurement of TiO<sub>2</sub> under UV irradiation in the presence of 2-propanol is applicable to in situ observation of a photocatalytic reaction, and the present study is a first step for the development of in situ observation system.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.catcom.2016.04.017>.

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