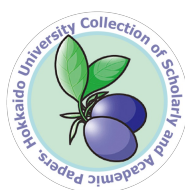




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| Author(s)        | Amano, Fumiaki; Tanaka, Masako; Ohtani, Bunsho                                                                                          |
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# Alkali Metal Ion-Modified Vanadium Mononuclear Complex for Photocatalytic Mineralization of Organic Compounds

Fumiaki Amano<sup>1,2</sup>, Masako Tanaka<sup>2</sup>, Bunsho Ohtani<sup>1,2</sup>

<sup>1</sup> Catalysis Research Center, Hokkaido University, Sapporo 001-0021, Japan

<sup>2</sup> Graduate School of Environmental Science, Hokkaido University, Sapporo 060-0810, Japan

## Abstract

Modification of silica-supported vanadium oxide (VS) photocatalysts with alkali metal ions enhanced the photocatalytic activity of the vanadium(V) mononuclear complex for oxidative decomposition of gaseous organic compounds into carbon dioxide. Action spectrum analysis revealed that the onset wavelength for cesium-ion-modified VS was 420 nm, which was ca. 20 nm longer than that with a titania photocatalyst, P25.

**Keywords:** Highly dispersed metal oxides, Cesium ion, V<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub>, Single-site photocatalyst, Charge-transfer excited state

## 1. Introduction

Photocatalytic oxidative decomposition of gaseous organic pollutants into carbon dioxide (CO<sub>2</sub>) is a useful technique for purification of indoor air. Recently, titanium-oxygen-cerium complexes supported on mesoporous silica have been reported to induce oxidation of gaseous 2-propanol under visible light irradiation [1]. Such all-inorganic complex photocatalysts could be further tuned and manipulated at a molecular level to be highly active photocatalysts. Mononuclear complexes supported on metal-oxide supports such as silica and zeolite have been shown to induce photocatalytic reactions such as partial oxidation of organic compounds and

reduction of nitrogen oxides with hydrocarbons [2-5]. However, these supported complexes seem less active for complete oxidative decomposition, i.e., mineralization, of organic pollutants because of the localized nature of the photoexcited state to induce one-electron transfer. Thus, the principle is different from that of a semiconductor photocatalyst, which could induce multi-electron transfer reactions. Indeed, a tetrahedrally coordinated vanadium mononuclear complex supported on silica, which is produced by dehydration of silica-supported vanadium oxide (VS), was effective for selective partial oxidation of alkanes and alkenes rather than for complete oxidation into CO<sub>2</sub> [6-8]. This is the reason why the application of mononuclear-complex photocatalysts has not been possible for oxidative decomposition of gaseous organic pollutants. In the present study, we investigated the photocatalytic activity of vanadium mononuclear-complex on silica for oxidative decomposition of acetaldehyde in air. Although an isolated bare complex was unstable in the presence of polar molecules and the photocatalytic activity was not high, modification by an alkali metal ion enhanced the stability of the mononuclear-complex structure and the photocatalytic activity for complete decomposition of acetaldehyde into CO<sub>2</sub>. The photocatalytic activity was comparable to that of the representative titania photocatalyst P25 under irradiation at wavelengths > 300 nm and much higher than that of P25 under irradiation at wavelengths > 370 nm.

## 2. Experimental section

The powder of VS was prepared by impregnation of an aqueous solution of ammonium vanadate (NH<sub>4</sub>VO<sub>3</sub>) into amorphous silica (AEROSIL-380), followed by evaporation to dryness. Cesium-ion-modified VS (CsVS) was prepared with an aqueous solution containing cesium carbonate (Cs<sub>2</sub>CO<sub>3</sub>) and NH<sub>4</sub>VO<sub>3</sub>. The amount of vanadium was adjusted to 2 atom% or 4 atom% to the total of vanadium and silicon, V/(V+Si). The atomic ratio of cesium to vanadium (Cs/V) was adjusted to 1.2. The dried silica powder (0.5 g) was poured in the corresponding solution (6 mL) heated on a hot plate at ca. 353 K, and the resulting suspension was stirred with a glass rod until dryness. After further drying at 393 K, the sample was calcined at 773 K for 2 h in air.

Photocatalytic decomposition of acetaldehyde was carried out using 100 mg of a photocatalyst powder spread on a glass plate (15 mm × 15 mm), which was placed on the bottom of a glass vessel connected to a closed gas circulation system. Air in the vessel was evacuated, and 60 Torr (1 Torr = 133.322 Pa) of dry air or ambient air was introduced to the system. At 60 min after injection of ca. 30 μmol acetaldehyde, photoirradiation was started using a 300-W xenon arc lamp ( $\lambda > 300$  nm) with a cut-off filter (Asahi Techno Glass L39,  $\lambda > 370$  nm) at room temperature. The amounts of acetaldehyde and CO<sub>2</sub> in the gas phase were measured by gas chromatographs. Action spectrum analysis was carried out for photocatalytic reaction under monochromatic light irradiation using a JASCO CRM-FD diffraction grating-type illuminator. A photocatalyst film was prepared on a glass plate (9 mm × 38 mm) with 30 mg of CsVS or 10 mg of P25 (Nippon Aerosil) titania. Initial rate of CO<sub>2</sub> liberation was measured to calculate apparent quantum efficiency assuming a five-electron (hole) process for evolution of one CO<sub>2</sub> molecule [9]. Diffuse reflection spectra were recorded using barium sulfate as a standard material on a JASCO V-670 UV-visible spectrophotometer equipped with a PIN-757 integrating sphere. Photoluminescence spectra were recorded on a JASCO FP-777 fluorescence spectrophotometer at a temperature < 104 K under vacuum.

### 3. Results and discussion

Figure 1 shows diffuse reflection spectra of VS, dehydrated VS (VS-dh), CsVS, and vanadium(V) oxide (Wako, V<sub>2</sub>O<sub>5</sub> 99%). VS-dh was prepared by evacuation of VS at 623 K for 1 h. The color of VS was changed from orange to white by the dehydration treatment, suggesting structural change of a V<sub>2</sub>O<sub>5</sub>-like cluster into a vanadium mononuclear complex with a terminal V=O bond and three V–O bonds bound to the silica surface (tetrahedral O=V(–O–Si)<sub>3</sub>) [10]. It is well known that the structure of vanadium oxide species supported on silica depends on the environment, and a vanadium mononuclear complex on silica could be reversibly changed to V<sub>2</sub>O<sub>5</sub>-like clusters in the presence of polar molecules such as water and methanol [10,11].

Interaction of VS-dh with acetaldehyde at room temperature changed the color from white to light yellow (Fig. 1e). This red-shift of photoabsorption was similar to that reported for interaction with methanol [10], suggesting formation of  $V_2O_5$ -like clusters. On the other hand, the color of CsVS was hardly changed even in the presence of polar molecules. The local structure of VS modified with an alkali metal ion such as rubidium ion has been investigated by X-ray absorption spectroscopy and reported as follows: 1) a tetrahedrally coordinated vanadium complex on silica exhibits two kinds of V–O bonds with two short bonds and two long bonds, 2) an alkali ion interacted with a vanadium complex, and 3) the positions of alkali ions are in disorder [12]. The proposed structure of the surface vanadate species was a vanadium mononuclear complex with two V–O bonds that interacted with an alkali metal ion and two V–O bonds bound to the silica surface.

Figure 2 shows time courses of  $CO_2$  liberation through photocatalytic oxidative decomposition of acetaldehyde in dry air. Under irradiation at wavelengths  $> 300$  nm, VS and VS-dh slowly induced decomposition of acetaldehyde into  $CO_2$ . The photocatalytic activity of VS-dh was slightly higher than that of VS, though the color of VS-dh changed from white to yellow after introduction of acetaldehyde as mentioned above. The  $CO_2$  liberation rate increased in the order of  $V_2O_5 < VS < VS\text{-}dh$ , suggesting that a highly dispersed vanadium oxide species on silica is more active than  $V_2O_5$  particles. On the other hand, white-colored CsVS showed much higher activity than those of VS and VS-dh, and the color did not change during the reaction. An almost stoichiometric amount of  $CO_2$  was liberated in the gas phase. We found that CsVS can also induce oxidative decomposition of acetaldehyde under irradiation with wavelengths  $> 370$  nm, while VS and VS-dh show negligible activity for  $CO_2$  liberation under similar conditions. Enhanced photocatalytic activity was achieved by interaction of cesium ion with vanadium complexes on silica. This effect was also found with other alkali metal ions such as potassium and rubidium. The atomic ratio of alkali metal to vanadium had to be greater than unity. It should be noted that CsVS was found to be effective for reactions under ambient air containing water vapor, though the rate of  $CO_2$  liberation decreased a little (c' of Fig. 2B).

Figure 3 shows photoluminescence spectra recorded at a temperature  $< 104$  K for CsVS and VS under vacuum. Phosphorescence from a vanadium mononuclear complex on silica has been investigated and the lifetime has been shown to be a few tens of milliseconds at 77 K [13,14]. The emission spectrum of VS exhibited fine structures due to transition from the ground vibrational level of the triplet excited state to vibrational levels of the ground state. The width of the vibrational bands is assignable to the frequency of a terminal V=O bond of the photoexcited mononuclear complex on silica [13,14]. On the other hand, CsVS shows an emission spectrum with no vibrational fine structures, suggesting interaction of alkali ions with the vanadium complexes. The onset wavelength in the excitation spectrum of CsVS (410 nm) was longer than that of VS (370 nm). This is consistent with results showing that alkali-ion-modified VS excited at 400-nm light emits phosphorescence as reported by Takenaka et al. [15,16]. The excitations are assignable to transition from O 2p nonbonding orbitals to  $\pi^*$ -like molecular orbitals of V=O and O–V–O moiety for VS and potassium-ion-modified VS (KVS), respectively [17]. Calculation by density functional theory indicates that the transition energy for KVS is lower than that for VS, suggesting excitation of KVS at longer wavelengths. Considering no appreciable photocatalytic activity of VS under irradiation with wavelengths  $> 370$  nm, excitation to the photoexcited triplet state of a vanadium mononuclear complex would be essential for photocatalytic reactions.

The photocatalytic activity of CsVS was compared with that of titania P25, a de facto standard commercial photocatalyst exhibiting a high level of activity, for photocatalytic oxidative decomposition of acetaldehyde in ambient air with relative humidity higher than 30%. Figure 4 shows the time courses of the amounts of acetaldehyde and CO<sub>2</sub> in the gas phase. In the dark, acetaldehyde was adsorbed on the photocatalyst immediately after injection. The amount of acetaldehyde adsorbed on P25 was larger than that of CsVS, although the specific surface area of P25 ( $48 \text{ m}^2 \text{ g}^{-1}$ ) was smaller than that of CsVS ( $208 \text{ m}^2 \text{ g}^{-1}$ ). The difference in the adsorption amount might be related to the acid-base property of surfaces, since acetaldehyde is considered to behave as a base or very weak acid and modification by alkali ions would provide a moderate basic

property. After commencement of photoirradiation, CO<sub>2</sub> was liberated by oxidative decomposition of the adsorbed acetaldehyde on the photocatalyst surface and gaseous acetaldehyde disappeared completely. The rate of CO<sub>2</sub> liberation over CsVS was comparable to that of P25 under irradiation at wavelengths > 300 nm and much higher than that of P25 under irradiation at wavelengths > 370 nm. On the contrary to the case for P25, the amount of CO<sub>2</sub> liberated in the gas phase for CsVS was not consistent to that expected for quantitative mineralization even after prolonged photoirradiation. This is probably due to the adsorption of CO<sub>2</sub> on the surface with basic property. We confirmed that CsVS was an effective photocatalyst for complete decomposition of not only acetaldehyde but also other organic compounds such as 2-propanol and acetone (data not shown).

The photoabsorption of CsVS and that of P25 were similar as shown in diffuse reflection spectra (Fig. 5). In order to analyze their action spectra, apparent quantum efficiency (QY) was measured for photocatalytic reaction with monochromatic irradiation. The action spectra of reaction by P25 and CsVS showed onset wavelengths of 400 nm and 420 nm, respectively. It has been reported that the active crystalline phase of titania photocatalysts of mixed anatase and rutile crystallites differs depending on the kind of photocatalytic reaction [18]. Since the flat-band potential of anatase (band gap of 3.2 eV) is shifted negatively by 0.2 V with regards to that of rutile (band gap of 3.0 eV) [19], one-electron reduction of molecular oxygen is expected to be possible for anatase but not for rutile. The action spectrum of P25 for decomposition of acetic acid was blue-shifted by ca. 30 nm from the diffuse reflection spectrum, indicating that rutile, which exhibits a photoabsorption edge at around 410 nm, contained in P25 was not effective for the reaction. This would be the reason why the photocatalytic activity of CsVS was higher than that of P25 when light of wavelengths > 370 nm was irradiated, although the photoabsorption spectra resembled each other.

#### **4. Conclusion**

A vanadium mononuclear complex photocatalyst on silica was not effective for photocatalytic oxidative decomposition of acetaldehyde into CO<sub>2</sub>, probably since the isolated complexes are easily aggregated into V<sub>2</sub>O<sub>5</sub>-like species in the presence of polar molecules. On the other hand, a vanadium complex interacting with an alkali metal ion was stable during the reaction and exhibited a high level of photocatalytic activity comparable to that of P25 for complete decomposition of acetaldehyde even in the presence of water vapor. Since the alkali metal ion-modified vanadium complex could be excited to the photocatalytic active state by photoabsorption at 370–410 nm, CsVS exhibited a CO<sub>2</sub> liberation rate much higher than that of P25 when the photoirradiation wavelength was longer than 370 nm.

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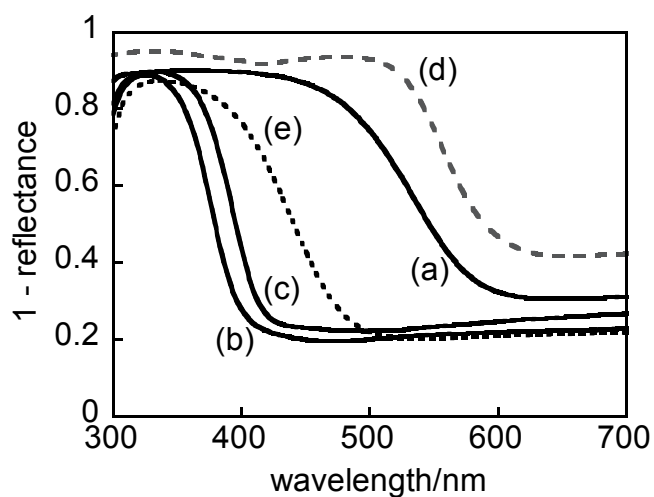


Fig. 1 Diffuse reflection spectra of (a) VS, (b) VS-dh, (c) CsVS, (d)  $V_2O_5$  particles, and (e) VS-dh in the presence of acetaldehyde.

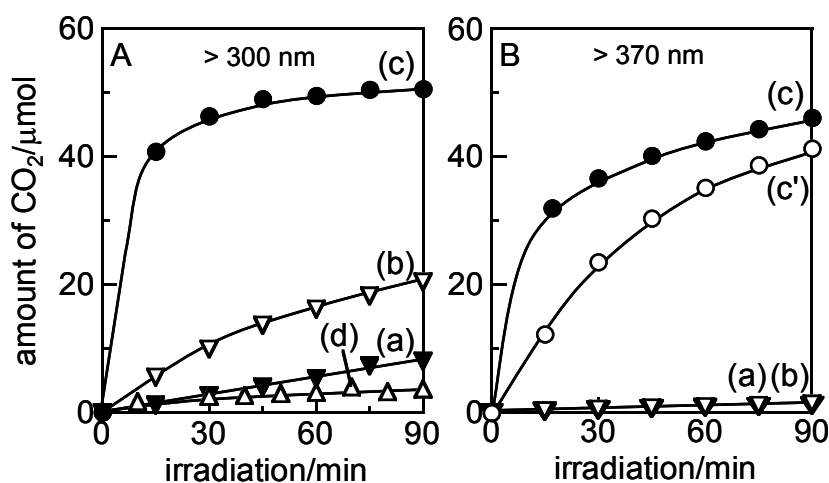


Fig. 2 Liberation of  $CO_2$  through oxidative decomposition of acetaldehyde (ca.  $30 \mu\text{mol}$ ) in dry air over (a) VS, (b) VS-dh, (c) CsVS, and (d)  $V_2O_5$  particles under irradiation at wavelengths longer than (A) 300 nm and (B) 370 nm. Plot (c') shows the results of photoirradiation of CsVS in ambient air with relative humidity of 30%.

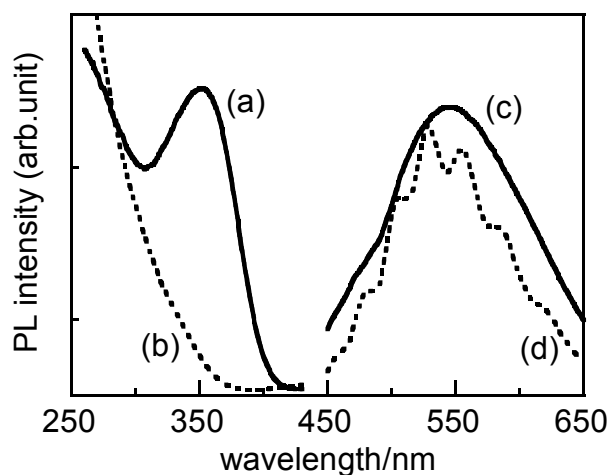


Fig. 3 Photoluminescence excitation spectra of (a) CsVS monitored at 540 nm and (b) VS monitored at 530 nm, and photoluminescence spectra of (c) CsVS excited at 350 nm and (b) VS excited at 300 nm.

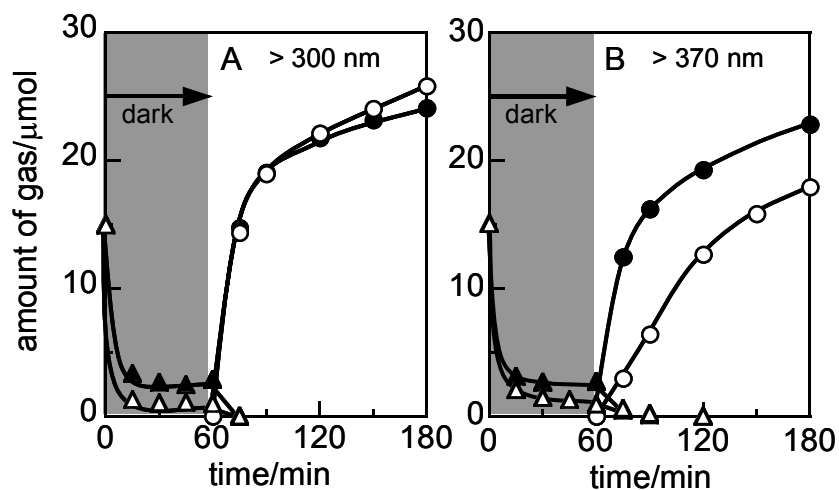


Fig. 4 Liberation of  $\text{CO}_2$  through oxidative decomposition of acetaldehyde (ca.  $15 \mu\text{mol}$ ) in ambient air over CsVS (closed symbols) and titania P25 (open symbols) under irradiation at wavelengths longer than (A) 300 nm and (B) 370 nm: acetaldehyde (triangles) and  $\text{CO}_2$  (circles).

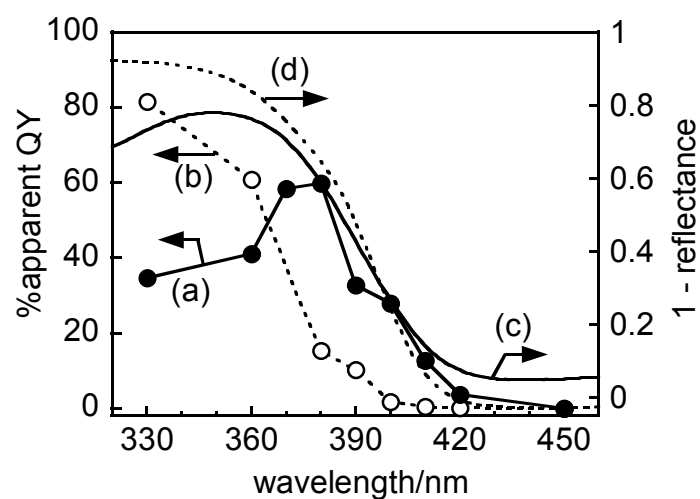


Fig. 5 Action spectra of (a) CsVS and (b) titania P25 for photocatalytic oxidative decomposition of acetaldehyde in ambient air. Diffuse reflection spectra of (c) CsVS and (d) titania P25.