Complete oxidation of acetaldehyde and toluene over a Pd/WO_3 photocatalyst under fluorescent- or visible-light irradiation

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Acetaldehyde was completely oxidized to CO_2 over a Pd/WO_3 photocatalyst under fluorescent-light irradiation in a flow-type reactor, and Pd/WO_3 was also used to completely oxidize toluene to CO_2 in a batch reactor under visible-light irradiation.

Photocatalysis with sunlight or indoor light has the potential to be a beneficial technology for the degradation of harmful volatile organic compounds (VOCs) such as formaldehyde, acetaldehyde, and toluene. For indoor applications, the fraction of UV light available is very low; therefore, visible-light-responsive photocatalysts are needed instead of UV-responsive photocatalysts such as TiO_2. Many semiconductor photocatalysts, particularly those based on TiO_2 (such as $TiO_{2-x}M_x$ [M = N, C, S, metals]), have been intensively investigated; however, so far, their ability to "completely oxidize organic compounds to CO_2" under visible light has not been satisfactory. WO_3 is a visible-light-responsive photocatalyst, and we previously reported that composite photocatalysts such as $CuBi_2O_4/WO_3$[1] and CuO/WO_3[2] efficiently catalyze the complete oxidation of acetaldehyde under visible light. In addition, the photodegradation of 2-propanol over Cu(II)-grafted WO_3 was reported by Irie *et al.*[3] The use of Pt as a co-catalyst also increases the photodegradation activity of WO_3.[2,4–7] Pt(2 wt%)/WO_3 shows higher activity than CuO(2 wt%)/WO_3 for the oxidation of acetaldehyde;[2] however, Pt is too expensive for indoor applications. In this study, we found Pd to be one of the most effective co-catalysts except for Cu compound and Pt metal and paid our attention to Pd because the cost of Pd is approximately one-fifth that of Pt. We optimized the Pd/WO_3 ratio and then compared the activity of Pd/WO_3 with the activities of bare WO_3, CuO/WO_3, nitrogen-doped TiO_2 (N-TiO_2), and TiO_2 in a batch reactor. We also photodegraded acetaldehyde in a flow-type reactor under fluorescent-lamp irradiation. Furthermore, toluene, which is a very persistent VOC, was photodegraded in a batch reactor under visible light.

WO_3 powder (surface area *ca.* 5 $m^2\ g^{-1}$), obtained from Wako Pure Chemical Industries, was used as a photocatalyst. Various co-catalyst powders (Pt, Pd, Cu and so on) were thoroughly mixed with WO_3 powder in a mortar. N-TiO_2, prepared as reported by Irokawa *et al.*,[8] and TiO_2 (Degussa, P-25) were used as the reference photocatalysts. Acetaldehyde, acetic acid, and toluene were photocatalytically degraded under the same conditions (in a batch reactor) with irradiation by a solar-simulating Xe lamp (the intensity is similar to 1 sun, AM 1.5 mainly at 400–600 nm) through a UV-cutoff filter (HOYA L-42), as previously reported.[2] Photocatalytic degradation of acetaldehyde was also carried out in a flow-type reactor consisting of a stainless steel cell with an acrylic plate and a window made of Pyrex glass. A slide glass plate was coated with the photocatalysts by means of the doctor blade method. Acetaldehyde gas was diluted to *ca.* 5 ppm with humid air (*ca.* 50% humidity). The flow rate was adjusted to 50 ml min^{-1}. A neutral white fluorescent lamp (National, FPL13EX-N) was used as the light source, and the illumination intensity on the photocatalyst film (*ca.* 60 cm^2) was adjusted to *ca.* 3000 lux. The amounts of acetaldehyde consumed and CO_2 generated during the reaction were measured with a gas chromatograph (Shimadzu, GC-2014) with a flame ionization detector equipped with a methanizer.

Acetaldehyde was photodegraded over WO_3 mixed with 2 wt% of various co-catalysts (Cu, Ru, Rh, Pd, Ag, Ir, Pt, Au, V_2O_5, Cr_2O_3, MnO_2, Fe_2O_3, CoO, NiO, CuO, ZnO, PdO, Ag_2O, and RuO_2) in the batch reactor under visible-light irradiation. The activities of the catalysts were evaluated in terms of the amount of CO_2 generated during the photodegradation reactions. Complete oxidation catalyzed by WO_3 was promoted only when co-catalysts containing Pt, Pd, or Cu were used. Pd nano-powder (Aldrich Co.) was particularly effective as a co-catalyst; therefore, we determined the optimum Pd/WO_3 ratio, which was 0.1 wt%.

The activity of Pd(0.1 wt%)/WO_3 for photodegradation of acetaldehyde is compared with the activities of bare WO_3, CuO(2 wt%)/WO_3, Pd(0.1 wt%)/N-TiO_2, N-TiO_2, and P-25 in Fig. 1. The amount of CO_2 produced over bare WO_3 was about half the amount of CO_2 expected for complete oxidation of the introduced acetaldehyde, because stable by-products such as acetic acid, formic acid, and formaldehyde accumulated on the bare WO_3.[1] In contrast, acetaldehyde was completely oxidized over Pd(0.1 wt%)/WO_3. The rate of CO_2 generation over the Pd/WO_3 catalyst was more than twice that over CuO(2 wt%)/WO_3 and nine times that over N-TiO_2. The activity of Pd/WO_3 was also compared with that of N-TiO_2 mixed with Pd at the same ratio (0.1 wt%). Pd(0.1 wt%)/WO_3 also showed higher activity than Pd(0.1 wt%)/N-TiO_2 and the

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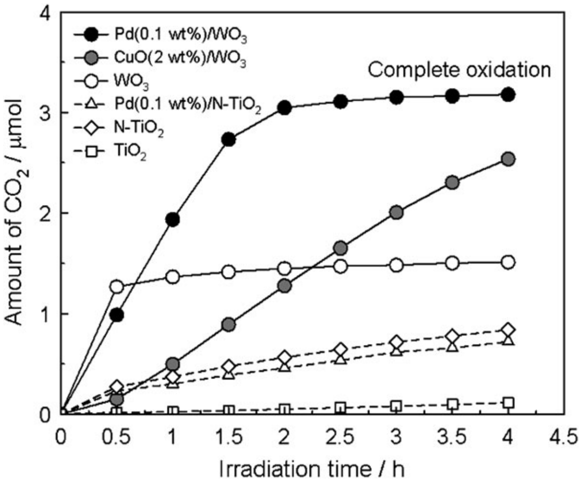

Fig. 1 Time courses of CO_2 formation during photodegradation of acetaldehyde (*ca.* 1.6 μmol) over various catalysts under visible-light irradiation (λ >400 nm).

activity of N-TiO_2 was not improved by Pd loading. Matsuoka *et al.* reported that the activity of a WO_3 film coated with Pd by a sputtering method is almost as low as that of a bare WO_3 film in the photodegradation of acetaldehyde, and acetic acid is barely decomposed at all.[5] However, we found that WO_3 loaded with Pd nano-powder was very active for the decomposition of not only acetaldehyde but also acetic acid (Fig. 2).

The CO_2 generation rate over Pd(0.1 wt%)/WO_3 was more than 15 times that over bare WO_3 and four times that over CuO(2 wt%)/WO_3. Furthermore, the apparent quantum efficiency (QE_a) of CO_2 generation from acetic acid over Pd(0.1 wt%)/WO_3 at λ = 400 nm was calculated as *ca.* 40%. Abe *et al.* reported that QE_a of 1 wt% Pt photodeposited on WO_3 in the photodegradation of acetic acid is *ca.* 10%.[4] Simple comparison of QE_a values is difficult because the efficiency depends on the reaction conditions, such as the light intensity and the concentrations of organic substances.[9] Nevertheless, the QE_a value of Pd(0.1 wt%)/WO_3 was very high compared with those so far reported using other visible-light-responsive photocatalysts.

The conduction band level of WO_3 (+0.5 V *vs.* NHE) is more positive compared with the potential for the single-electron reduction of oxygen (O_2/O_2^- = −0.56 V *vs.* NHE; O_2/HO_2 = −0.13 V *vs.* NHE), and it is considered that the positive conduction band level is one of the reasons for the difficulty of O_2 reduction and the low photocatalytic activity of pure WO_3.[1–4] In the presence of Pt, it can proceed the O_2 reduction effectively by a multi-electron process (O_2/H_2O_2 = +0.68 V *vs.* NHE; O_2/H_2O = +1.23 V *vs.* NHE) as a catalyst and improved the WO_3-catalyzed photodegradation of organic substances totally.[3,4] Pd can also proceed multi-electron oxygen reduction as well as Pt.[10] In addition, we confirmed that formic acid and formaldehyde generated as intermediates in the photodegradation of acetic acid could be oxidized to CO_2 in the presence of Pd powder even in the dark, as is the case for Pt powder;[11] whereas acetic acid could not be decomposed in the dark. Furthermore, CuO powder showed no activity for the decomposition of acetic acid, formic acid and formaldehyde in the dark. Therefore, we considered that the ability of the co-catalyst to degrade the intermediates (formic acid and formaldehyde) into CO_2 under dark conditions is one of the reasons for the excellent activity of Pd(0.1 wt%)/WO_3 compared to that of CuO(2 wt%)/WO_3 in the photodegradation of acetic acid and acetaldehyde. However, it should be noted that the activity of N-TiO_2 was not improved by Pd loading. It is speculated that the intermediates generated in the photodegradation might be strongly adsorbed on the surface of N-TiO_2 and find it hard to reach the surface of Pd to react, or that the degradation of acetic acid and acetaldehyde might not proceed mainly *via* free formic acid and formaldehyde over N-TiO_2.

In addition, toluene, which is a very persistent VOC, was completely oxidized over Pd(0.1 wt%)/WO_3, and the catalytic activity was not decreased when the catalyst was reused (Fig. 3). In contrast, complete oxidation of toluene did not occur over bare WO_3.

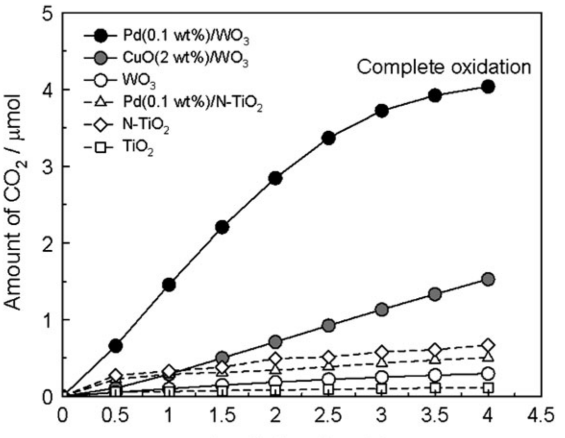

Fig. 2 Time courses of CO_2 formation during photodegradation of acetic acid (*ca.* 2 μmol) over various catalysts under visible-light irradiation (λ >400 nm).

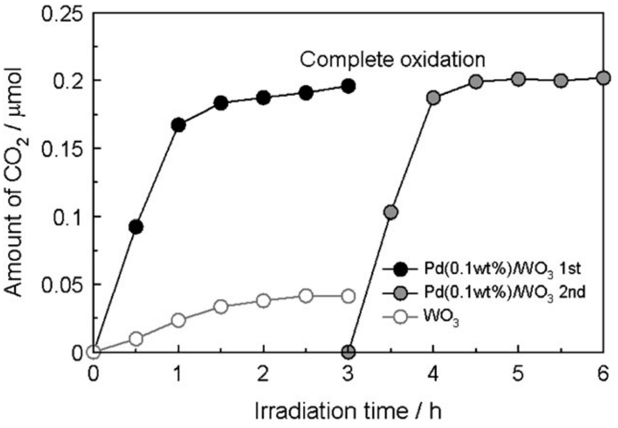

Fig. 3 Time courses of CO_2 formation during photodegradation of toluene (*ca.* 0.03 μmol) over various catalysts under visible-light irradiation (λ >400 nm). The catalysts were cleaned by means of a pre-photoreaction before measurement.

Table 1 Removal of acetaldehyde from flowing gas (5 ppm, 50 ml min^{-1}) over Pd(0.1 wt%)/WO_3, WO_3, and N-TiO_2 under fluorescent-lamp irradiation (*ca.* 3000 lux, 0.19 mW cm^{-2} at 400–450 nm)[a]

Photocatalyst	ARR [%]	RCO [%]	RCOA/mg m^{-2} h^{-1}
Pd(0.1 wt%)/WO_3	100	100	4.5
WO_3	92	80	3.3
N-TiO_2	76	13	0.4

[a] ARR: The acetaldehyde removal ratio. RCO: The ratio of complete oxidation of acetaldehyde to CO_2. RCOA: The rate of complete oxidation of acetaldehyde.

Acetaldehyde was also photodegraded in a flow-type reactor under fluorescent-lamp irradiation. The light intensity was *ca.* 3000 lux through an acrylic plate and a Pyrex glass window. The results are shown in Table 1.

In the case of the N-TiO_2, the acetaldehyde removal ratio (ARR) was 76%, and the ratio of complete oxidation of acetaldehyde to CO_2 (RCO) was only 13%; these values suggest that the acetaldehyde was not completely oxidized. WO_3 was more active than N-TiO_2, but again acetaldehyde was not completely oxidized. In contrast, Pd(0.1 wt%)/WO_3 catalyzed the complete oxidation of acetaldehyde (ARR = 100%; RCO = 100%), and the rate of complete oxidation of acetaldehyde (RCOA) was calculated to be *ca.* 4.5 mg m^{-2} h^{-1}. There are few reports that confirm complete oxidation in the flow-type reactor; therefore, it is very meaningful that stoichiometric CO_2 production was observed for the complete oxidation. In conclusion, Pd(0.1 wt%)/WO_3 was more active than bare WO_3 and N-TiO_2 both in a batch-type reactor and in a flow-type reactor; Pd/WO_3 is a promising new photocatalyst for purification of various environmental pollutants under visible-light or fluorescent-lamp irradiation.

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