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Photocatalytic Mineralization of Acetic Acid in Aqueous Suspension of Metal-loaded Cerium(IV) Oxide under Irradiation of Visible Light

Atsuhiro Tanaka, Keiji Hashimoto, and Hiroshi Kominami*
Department of Applied Chemistry, Faculty of Science and Engineering, Kinki University,
Kowakae, Higashiosaka, Osaka 577-8502

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Photocatalytic activity of cerium(IV) oxide (CeO_2) particles in decomposition of acetic acid in aqueous suspension was examined under irradiation of visible light. Acetic acid was decomposed to carbon dioxide (CO_2) and the rate of CO_2 formation was increased by loading of 0.1 wt% cocatalysts (Pt, Au, Rh, Ru, Pd, Ag, Cu, and Ir) on CeO_2 by photodeposition. Cocatalysts showed almost the same levels of enhancement of CO_2 evolution, i.e., Ag/CeO_2 and Cu/CeO_2 exhibited rates similar to that of Pt/CeO_2. The action spectrum revealed that decomposition of acetic acid was induced by photoabsorption of CeO_2.

Titanium(IV) oxide (TiO_2) photocatalysts have been used for removal of harmful compounds in air and water and are also expected to remediate air pollution in houses with volatile organic compounds (VOC), such as formaldehyde, causing sick house syndrome.[1] However, since the amount of UV light in living spaces is limited, photocatalytic performance of TiO_2 is insufficiently utilized. Therefore, many efforts have been devoted to synthesis of photocatalysts that respond to visible light, and various types of photocatalysts have been reported.[2–12] From energy and environmental points of view, catalysts consuming less energy and other chemicals and yielding less waste and/or by-product(s) in their preparation would be more environmentally friendly. A simple metal oxide that has a simple composition and structure shown as MO_x and that requires no additional activation and/or visiblization is a candidate for environmentally friendly photocatalysts. As far as we know, among simple oxides, only tungsten(VI) oxide has been reported to exhibit photocatalytic activity in decomposition of organic compounds under irradiation of visible light.[6,7]

Cerium(IV) oxide (CeO_2) is an indispensable compound in various fields as a catalyst material, abrasive for chemical mechanical polishing, UV absorber, fluorescent material, and pigment because of its chemical, physical, optical, and electric properties, i.e., high chemical stability, nontoxicity, high thermal stability, redox, and photoabsorption properties. Even in catalysis, CeO_2 is used as a key material of an oxidation catalyst for diesel soot removal, dehydration catalyst for alcohols, cocatalyst for a dehydrogenation catalyst, support for metal catalysts such as catalysts for preferential carbon monoxide oxidation and oxygen storage material for an automotive three-way catalysts.[13] In contrast to the wide applications to (thermo)catalyst materials, there are only a few reports on application of CeO_2 to photocatalytic materials,[14–17] although CeO_2 possesses semiconducting and UV-photoabsorbing properties.

In this study, we investigated CeO_2 as a photocatalyst and found that CeO_2 and metal-loaded CeO_2 exhibited photocatalytic activity for mineralization of acetic acid in an aqueous suspension under irradiation of visible light.

Commercial CeO_2 powder (Nanotech^R) having a cubic structure and a large specific surface area ($47\,m^2\,g^{-1}$) was supplied by Kanto Chemical. Loading of metals (Cu, Ru, Rh, Pd, Ag, Ir, Pt, and Au) on CeO_2 was performed by photodeposition. Bare CeO_2 powder (150 mg) was suspended in water ($10\,cm^3$) in a test tube, and the test tube was sealed with a rubber septum under argon (Ar). Aqueous solutions of oxalic acid (100 µmol) and a metal source (as 0.1 wt% metal) were injected into the sealed test tube and then photoirradiated at $\lambda > 300\,nm$ with a 400-W high-pressure mercury arc (Eiko-sha, Osaka, Japan) under Ar with magnetic stirring in a water bath continuously kept at 298 K. The metal source was reduced by photogenerated electrons, and the metal was deposited on CeO_2 particles, resulting in the formation of metal-loaded CeO_2. Analysis of the liquid phase after the photodeposition revealed that each metal source was almost completely (>99.9%) deposited as metal on the CeO_2 particles. The resultant powder was washed repeatedly with distilled water and then dried at 310 K overnight under air. Hereafter, the metal-loaded CeO_2 sample is designated as M/CeO_2, (M: deposited metal). The dried M/CeO_2 powder (50 mg) was suspended in distilled water ($5\,cm^3$), bubbled with O_2, and sealed with a rubber septum. Acetic acid (50 or 4 µmol) was injected into the suspension and then irradiated with visible light of a 400-W xenon (Xe) lamp (Ushio, Tokyo, Japan) filtered with an L-42 filter (Asahi Technoglass, Chiba, Japan) with magnetic stirring in a water bath continuously kept at 298 K. Light irradiated to the reaction system is shown in Figure 1. The amount of carbon dioxide (CO_2) in the gas phases of reaction mixtures was measured using a Shimadzu GC-8A gas chromatograph equipped with Porapak QS (CO_2) columns.

Powder X-ray diffraction (XRD) of the CeO_2 sample revealed that the sample consisted of cubic phase (ICDD No. 43-1002). Crystallite size of the CeO_2 sample was calculated to be 22 nm from the half-height line width by the Scherrer method. In the XRD pattern of 0.1 wt% M/CeO_2, peaks attributed to the metals were not observed, indicating that each metal was finely dispersed on the surfaces of CeO_2 particles. Figure 1 shows the absorption spectrum of CeO_2. For comparison, the spectrum of commercial TiO_2 (Degussa P25, $50\,m^2\,g^{-1}$) is also shown in Figure 1. Strong photoabsorption was observed at $\lambda < 425\,nm$ in the spectrum of CeO_2, and the band gap was estimated to be 2.9 eV. In fact, the color of the present CeO_2 sample was yellow; therefore, photocatalytic activity of CeO_2 under visible light irradiation was expected.

Figure 2 shows the time courses of evolution of CO_2 from aqueous solutions of acetic acid in the presence of bare and Pt-, Ag-, and Cu-loaded CeO_2 samples (0.1 wt% each) under

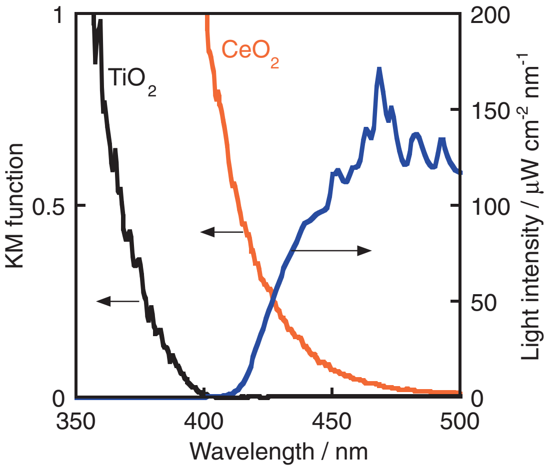

Figure 1. Absorption spectra of CeO_2 and TiO_2(P25) (left axis) and light irradiated to the reaction system (right axis).

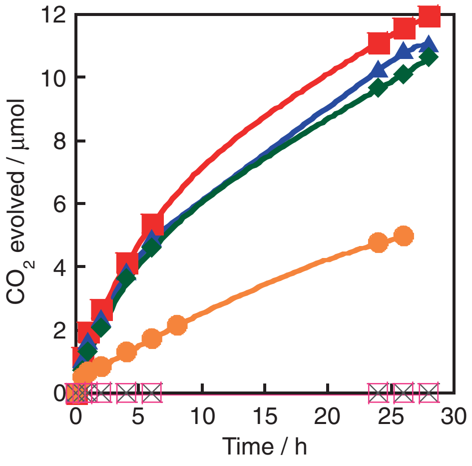

Figure 2. Time courses of evolution of CO_2 from aqueous solutions of acetic acid (50 μmol) in the presence of CeO_2 (circles), Pt/CeO_2 (closed squares), Ag/CeO_2 (triangles), Cu/CeO_2 (diamonds), TiO_2 (open squares), and Pt/TiO_2 (crosses) under irradiation of visible light.

irradiation of visible light. For comparison, results for TiO_2(P25) and Pt/TiO_2(P25) are also shown. No CO_2 was evolved in either the case of TiO_2(P25) or Pt/TiO_2(P25). The former result indicates that visible light coming from a filtered Xe lamp did not induce photocatalytic reaction by TiO_2. From the latter result, we can conclude that thermocatalysis of Pt loaded on TiO_2 was negligible at 298 K. On the other hand, CO_2 was evolved in the presence of bare CeO_2 just after irradiation of visible light, and formation of CO_2 continued with irradiation time. We also confirmed that no color change in CeO_2 during the photoirradiation and no dark reaction (thermocatalytic reaction) occurred in the presence of CeO_2. These results indicate that bare CeO_2 worked as a photocatalyst for decomposition of acetic acid under irradiation of visible light and are in contrast to the results for bare WO_3 showing that WO_3 is deactivated due to self-reduction of W^{6+} to W^{5+} by photogenerated electrons. This difference in the behaviors of CeO_2 and WO_3 suggests that the level of the conduction band (CB) of CeO_2 was slightly higher than the CB of WO_3 and that one-electron reduction of oxygen occurred in the case of CeO_2 but not in the case of WO_3. Loading of Pt or Pd particles on WO_3 powder enables photocatalytic mineralization of organic compounds in water to occur probably because these metals work as catalysts for two- or four-electron reduction of oxygen easily occurring by electrons with lower potential.[6,7] In the case of CeO_2, the photocatalytic activity was also improved by only a small amount (0.1 wt %, optimized) of Pt loading as shown in Figure 2 for the same reason as that in the case of WO_3. It should be noted that Ag, which is much cheaper than Pt, and Cu, a popular base metal, showed almost the same cocatalyst effects on photocatalytic decomposition as Pt did. Effects of other metals as cocatalysts on photocatalytic decomposition of acetic acid (as CO_2 evolution for 24 h) are summarized in Table 1. Effects of Ag and Cu were parallel with those of Pd and Au and larger than those of Rh and Ru.

Table 1. Evolution of CO_2 for 24 h from acetic acid (50 μmol) in aqueous suspensions of various photocatalysts under irradiation of visible light

Photocatalyst	Metal source	CO_2 evolved /μmol
TiO_2	—	≈0
Pt/TiO_2	H_2PtCl_6	≈0
CeO_2	—	4.8
Pt/CeO_2	H_2PtCl_6	11.1
Au/CeO_2	$HAuCl_4$	10.7
Rh/CeO_2	$RhCl_3$	8.6
Ru/CeO_2	$RuCl_3$	8.9
Pd/CeO_2	$PdCl_2$	10.0
Ag/CeO_2	$AgNO_3$	10.3
Cu/CeO_2	$CuCl_2$	9.7
Ir/CeO_2	$IrCl_3$	7.9

To obtain an action spectrum in this reaction system, mineralization of acetic acid in an aqueous suspension of Pt/CeO_2 was carried out at 298 K under irradiation of monochromated visible light from a Xe lamp with light width of ±5 nm. Apparent quantum efficiency (AQE) at each centered wavelength of light was calculated from the ratio of the amount of CO_2 and the amount of photons irradiated, using the following equation:

$$\mathrm{AQE} = \frac{\text{amount of } CO_2}{\text{amount of incident photons}} \times 100 \qquad (1)$$

Figure 3 shows the results. The apparent quantum efficiency was in agreement with the photoabsorption (1 − [reflectance]) of CeO_2, indicating that photoabsorption of visible light by CeO_2-induced decomposition of acetic acid, i.e., photocatalytic reaction actually occurred in the present conditions.

To confirm stoichiometry of the decomposition of acetic acid in the present system, Pt/CeO_2 was used for a long time and it continuously decomposed acetic acid without losing its activity (Figure 4). After irradiation for 50 h, CO_2 evolution was almost saturated at around 8 μmol, which corresponded to the initial amount of acetic acid (4 μmol), indicating that acetic acid was almost completely decomposed to CO_2 ($CH_3COOH + 2O_2 = 2CO_2 + 2H_2O$) under irradiation of visible light in the presence of Pt/CeO_2.

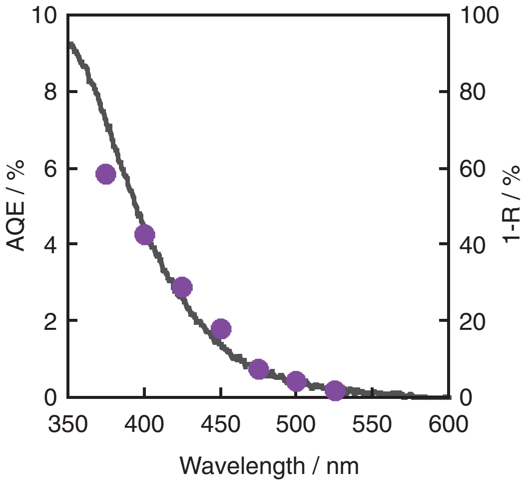

Figure 3. Absorption spectrum of 0.1 wt% Pt/CeO_2 measured with barium sulfate as a reference (right axis) and action spectrum (circle) in acetic acid decomposition (left axis).

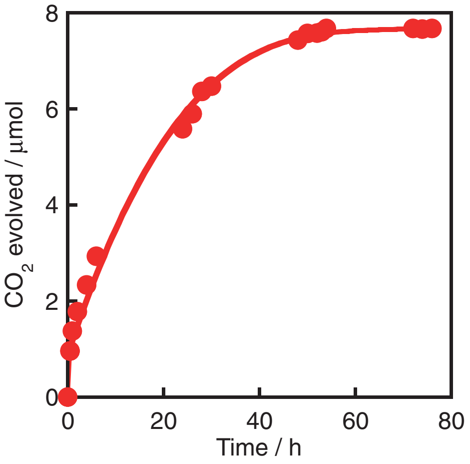

Figure 4. Time course of evolution of CO_2 from acetic acid (4 µmol) in an aqueous suspension of 0.1 wt% Pt/CeO_2 under irradiation of visible light.

In conclusion, CeO_2 works as a photocatalyst for mineralization of acetic acid in aqueous suspensions under irradiation of visible light. The reaction rate is increased by loading of 0.1 wt% cocatalysts on CeO_2, and Ag and Cu exhibit effects parallel with that of Pt.

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