Photocatalytic Activity of Au/TiO_x Particles Stimulated with Visible Light: Gas-phase Reactions of Formaldehyde, Acetaldehyde, and Phenol

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(Received November 1, 2007; CL-071207; E-mail: tajima-kazuo@kanagawa-u.ac.jp)

This document will communicate that the Au/TiO_x photocatalyst shows a high activity with tremendous efficiency for the degradation of volatile organic compounds, such as formaldehyde, acetaldehyde, and phenol, with visible light. Also, we found that photocatalytic degradation of phenol could take place in dry air as a carrier gas but not in Ar atmosphere.

The visible-light-sensitized catalyst based on TiO_2 (anatase) has been prepared with the various modifications; ion-doping,[1–5] sensitization with CdS or dyes,[6,7] and so on. Recently, we found that Au/TiO_x particles exhibited the photocatalytic activity with high degradation efficiency for an aqueous solution of Methyl Orange by irradiation with visible light over 470 nm in wavelength.[8] The preparation and properties of Au/TiO_x have been described in previous paper. The optimum composition of Au/TiO_x was consisted of 1(Au):300(Ti) in atomic ratio, and the sample was heated at 200 °C for 3 h in an oven. This document describes about the photocatalytic activity for the pollutant gas phases irradiated with visible light. If we examined photocatalytic reactants of Au/TiO_x complex particles in gas phase, the mechanism of decomposition will be clarified.

Each gas sample of formaldehyde, acetaldehyde, and phenol, which give rise to serious sick building syndrome, was prepared at 150 ppm in a fluorocarbon-made gas container bag ($15 \times 20\,cm^2$) with dry air or dry argon as a carrier gas at room temperature. The gas sample was carefully set on the stage of an irradiation apparatus (Luminar Ace LA-180Me, HAYASHI), which could be irradiated with visible light (Metal Halide Lump), illumination intensity of $30\,mW/cm^2$, after passing a glass-filter (VY-47, Toshiba). This filter cuts off the light less than 470 nm in wavelength. About 150 mg of the powdery Au/TiO_x catalyst was used for each catalytic reaction in the light pass inside of the container bag. The entire gas phase was stirred with a Teflon-coated magnetic spin bar. Photocatalytic degradation of the gases was performed as a function of irradiation time at constant light intensity. The criterion of degradation for the specimen gas was represented by a decrease of relative area in GC peaks detected by a gas chromatograph (GC) (GC4000, GL Science Co.) under the constant conditions. Special attention was paid at taking the sampling gas for GC after sufficiently mixing as a whole, because the irradiation with light was limited in some local place of the gas container bag.

Figure 1 shows the time course of photocatalytic degradation for acetaldehyde with and without irradiation of visible light in the presence or absence of Au/TiO_x catalyst. We found that acetaldehyde in the gas state was obviously decomposed with visible light by means of the powdery Au/TiO_x catalyst. Acetaldehyde molecules corresponding to 150 ppm could be almost 95% degradated in 5 h by irradiation with visible light over 470 nm. We could confirm that acetaldehyde could not be completely decomposed with no catalyst under irradiation of light and also with catalyst in the dark.

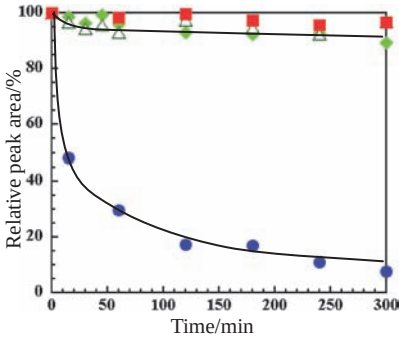

Figure 1. Time course of photocatalytic decomposition of acetaldehyde in gas phases. ●: catalyst with light, ◆: only light without catalyst, △: only catalyst without light, ■: catalyst with light in argon atmosphere.

Especially interesting phenomena were observed in the photocatalytic reaction in the presence of Au/TiO_x, where the carrier gas for acetaldehyde was switched to dry argon gas from air. Though the irradiation conditions in photoreaction registered no changes, acetaldehyde degradation could not be photocatalyzed. This phenomenon suggests that the photocatalytic degradation of acetaldehyde caused by the Au/TiO_x catalyst needs the coexistence of oxygen molecules. More detailed discussion will be made later in this paper.

Figure 2 shows the results of photocatalytic decomposition of phenol gas. The degradation rate seems to be almost the same as that of acetaldehyde gas under the same conditions, though benzene ring would be more chemically stable than acetaldehyde molecule for oxidation decomposition. In order to recognize the occurrence of photocatalytie decomposition of phenol by the Au/TiO_x catalyst, we measured the IR spectra for phenol gas before and after 3 h irradiation. Figure 3 shows the IR spectra

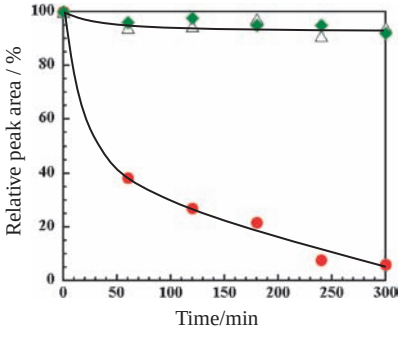

Figure 2. Time course of photocatalytic decomposition of phenol in gas phases. ●: catalyst with light, ◆: only light without catalyst, △: only catalyst without light.

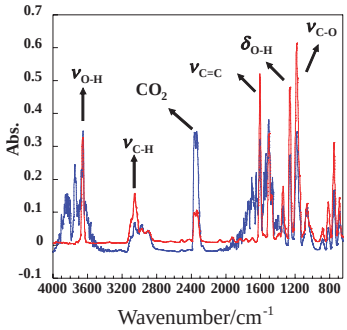

Figure 3. IR spectra for phenol before (red) and after (blue) photocatalytic decomposition by the Au/TiO_x catalyst by irradiation with visible light.

of phenol measured by the use of a gas cell (GAS-8M-VIR: JASCO).

In comparison of IR spectra before and after irradiating, the remarkable changes were the increased absorption peaks corresponding to carbon dioxide at 2300 cm^{-1}, the decreased absorption peaks for benzene ring at 1200 to 1600 cm^{-1}, and also for the peak of C–H stretching vibration at 3000 cm^{-1}. Moreover, we found a couple of peaks due to water vapor at 3500 to 3900 cm^{-1}. From absorption changes in these IR spectra, phenol molecules seem to be almost completely oxidized into CO_2 and H_2O molecules, as shown by solid red circles in Figure 2.

We found also that the plot of logarithmic relative peak area vs. time showed a good linear relation, such a first-order reaction for the degradation rate of acetaldehyde and phenol molecules as shown in Figure 4. The oxidation reactions of these organic molecules with Au/TiO_x catalyst may be caused by the presence of excess amount of oxygen molecules, similarly ester hydrolysis in water is a pseudo-first-order reaction. In other words, the present photocatalytic degradation occurs only under the presence of oxygen molecules in carrier gas, when both the Au/TiO_x catalyst and irradiation of light are employed at the same place and time. Therefore, we can say that the activity of Au/TiO_x particles works not as a chemical catalyst but as a photocatalyst.

The experimental finding of a pseudo-first-order reaction suggests that oxygen molecules may first be converted into active or radical oxygen on the surface of Au/TiO_x catalyst by irradiation with visible light, and subsequently active oxygen produced by such a way reacts with oxidizable compounds. The formation of active oxygen on the Au/TiO_x surface could

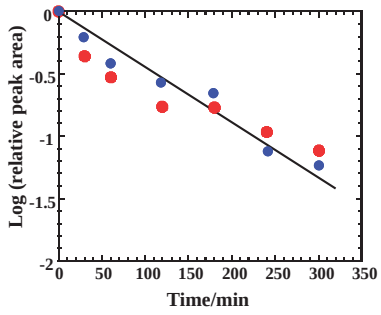

Figure 4. Plot of logrithmic relative peak area vs. time curve for the decomposition data of Figures 1 and 2.

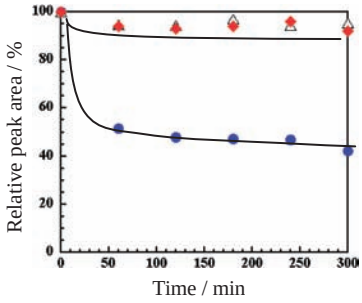

Figure 5. Time course of photocatalytic decomposition of formaldehyde in gas phases. ●: catalyst with light, ◆: only light without catalyst, △: only catalyst without light.

be expected from the experimental conditions such that the photocatalytic degradation was perforemed only in the coexistence of catalyst, oxygen, and visible light. We will provide more details about the active oxygen formation on the Au/TiO_x particle surfaces by irradiation with visible light elsewhere.

Figure 5 shows the results of photocatalytic degradation of formaldehyde gas under the same experimental conditions. It was made clear that the initial inclination of photocatalytic degradation curve did not differ significantly from the case of acetaldehyde or phenol but did not progress more than about 55% with respect to decomposition. Though the reason has not been made clear, the following equilibrium on the catalyst surface or in the reaction container bag seems to be probable:

$$HCHO + O_2^* \rightarrow CO_2 + H_2O \quad (1)$$

where O_2^* indicates the active oxygen molecule produced probably in the present photocatalystic reaction.

However, since acetaldehyde could almost completely decompose in the progress of time under the same conditions, formaldehyde or some intermediaries, e.g., HCOOH molecules, might hinder more the degradation progress. These molecules probably remain adsorbed on the surface of Au/TiO_x catalyst.

The Au/TiO_x catalyst, however, can be used repeatedly for the oxidation. Actually, we have tested the reproducibility of photocatalytic activity for an aqueous solution of Methyl Orange. As reported in a previous paper,[8] it takes a few hours to decompose it completely. The catalyst can be used through recycling several times, though the activity may gradually decline. However, after being used several times, if the used catalyst was refreshed by heating at 200 °C for 3 h, the catalyst activity may be completely recovered. So, we think that when formaldehyde gas is used, the apparent equilibrium takes place because some reaction products are strongly adsorbed on the catalyt surface and Au/TiO_x particles does not change into anatase.

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Published on the web (Advance View) February 16, 2008; doi:10.1246/cl.2008.330