Improvement of Catalyst Durability in Benzene Photooxidation by Rhodium Deposition on TiO_2

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Photocatalytic oxidation of benzene in air was carried out over TiO_2 and metal-loaded TiO_2 catalysts at room temperature. Deposition of Rh on TiO_2 improved the catalyst durability by inhibiting the formation of carbon deposits on the catalyst surface and accelerating their decomposition.

Air pollution with volatile organic compounds (VOCs) is one of the serious environmental problems. Hitherto, heterogeneous photocatalytic oxidation systems using TiO_2 catalysts have been extensively studied for the VOC removal in gas phase.[1] In this system, irradiation of semiconductors with UV or near-UV light generates highly reactive electron-hole pairs and initiates redox reactions decomposing the VOCs. The photocatalytic system has an advantage over other systems such as the thermal oxidation and catalytic incineration in that it can efficiently decompose the low concentration of VOCs under mild conditions without additive fuel. It has been reported that so many kinds of organic compounds including hydrocarbons, alcohols, halocarbons and amines decompose on the illuminated TiO_2.[2–6] In many cases, however, deactivation of TiO_2 has been generally observed during the photoreaction.[6] Therefore, the mechanism for the catalyst deactivation should be elucidated to practically utilize photocatalytic systems.

Benzene is an important feedstock and widely used. However, it is required to remove benzene from the flue gases from various sources, due to its carcinogenicity. We have carried out the photooxidation of dilute benzene with TiO_2 in air (80 – 250 ppm).[7,8] We showed that benzene decomposition was greatly suppressed with increasing the benzene concentration, due to the increasing amount of carbon deposits on the used catalyst.[7] We herein report that deposition of Rh on TiO_2 depresses the catalyst deactivation in the benzene photooxidation, by inhibiting the formation of carbon deposits on the catalyst and accelerating their decomposition.

TiO_2 P-25 was used as the catalyst and the precursor. The surface area of TiO_2 was 43 (m^2/g). Rhodium-deposited TiO_2 was prepared by the photodeposition method. TiO_2 powder was dispersed into an ethanol–water solution containing $RhCl_3 \cdot 3H_2O$ in a Pyrex vessel with vigorously stirring. N_2 gas was bubbled into the suspension to remove the dissolved O_2. The suspension was irradiated with a 500-W high-pressure Hg lamp for 2 h. After the irradiation, the resultant Rh-deposited TiO_2 powder was filtered off, washed with water, and dried at 110 °C.

Reactions were carried out with a flow reactor. The reactor used in this study was composed of an inner rod (8 mm outer diameter, 500 mm length) and an outer tube (13 mm inner diameter), which were fabricated from Pyrex glass. Catalysts were coated on the surface of the inner rod by wash coat techniques. It was surrounded by four 20-W black light bulbs. The reaction temperature was maintained approximately at 303 K. The catalyst was coated onto the inner rod from an aqueous slurry by the washcoat techniques and the rod was then dried at 383 K. Concentrations of CO_2 and CO were determined with a gas chromatograph equipped with a TCD, a FID and a methane converter. Benzene was determined with a GC. As a pretreatment, the catalyst was irradiated in humid air.

Figure 1 shows the time courses for the benzene photooxidation over TiO_2 and Rh/TiO_2 catalysts (benzene 250 ppm in air, relative humidity of 50%). No reaction took place in the dark. The reaction profiles were taken after the adsorption equilibrium was achieved between the gas phase and the catalyst surface in the photoreactor. In the initial period, benzene conversion for pure TiO_2 was about 70%. However, it rapidly decreased with time on stream, and reached a stationary value (13%) after about 180 min.

When Rh-deposited TiO_2 catalyst was used for the reaction, the conversion in the initial period was comparable with that for pure TiO_2. Although the conversion decreased with time, the decrement level was much smaller than that for the pure TiO_2. After about 10 h on stream, the conversion reached the stationary state and was about 3 times larger than that for pure TiO_2. Here, total amount of benzene reacted was estimated to be 3.0×10^{-4} mol. Turnover number for the benzene decomposition was estimated by taking the total amount of benzene reacted and normalized by the Ti density of the single crystal

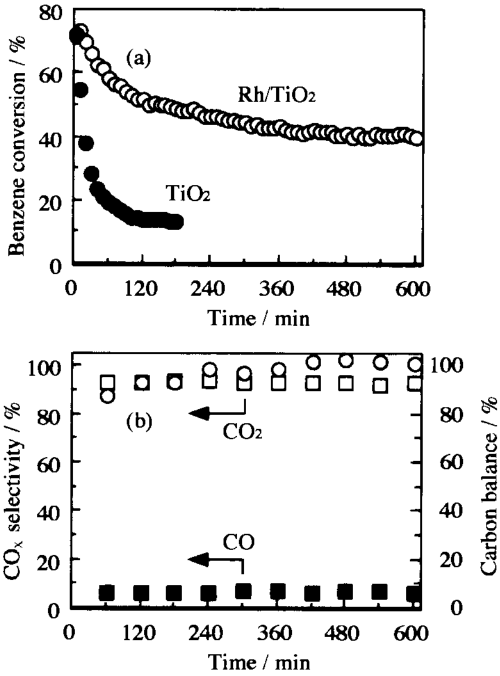

Figure 1. Time course for (a) the conversion and (b) the CO_x selectivity in benzene photooxidation. (□,■), CO_x selectivity; (○), carbon balance; benzene, 250 ppm; relative humidity, 50%; reaction temp, 30 °C; catalyst, 0.24 g.

surfaces of anatase (1.90–7.00 atoms/nm^2)[9] and the amount of Rh loaded (0.5 wt%). This led to 2.5–9.2 molecules per a Ti site and 25 molecules per a Rh site, showing that the reaction catalytically proceeded.

Benzene was oxidized to CO_2 and CO. Figure 1(b) shows the time courses for the selectivities to CO_2 and CO, and the carbon balance in the benzene photooxidation with Rh/TiO_2. The selectivities to CO_2 and CO were 94 and 6%, respectively. They were almost unchanged with time. The carbon balance was imperfect at the initial time. However, it reached the steady value in the range of 97–103% after about 4 h.

Table 1 summarizes the results of benzene photooxidation over metal loaded TiO_2 catalysts. The conversions were measured at the stationary state. Among these catalysts, Rh/TiO_2 was most effective for the reaction. The rate with Rh/TiO_2 was about 3 times higher than that with TiO_2. Deposition of Ir on TiO_2 had the negative effect on the reaction. On the other hand, deposition of Pt had almost no effect.

Deactivation of TiO_2 during the benzene photooxidation was ascribed to the formation of carbon deposits on the catalyst surface. TiO_2 was significantly browned by their formation during the reaction. The brownish carbon deposits decomposed to CO_x and the catalyst color was recovered to white by the irradiation in humid air without benzene. Figure 2 shows the formation behavior of CO_x in decomposing the carbon deposits on the used TiO_2 catalyst. There was an induction period for the CO_x formation, and it decreased with time. According to the time course plot, the amount of carbon deposits was estimated to be 241 μmol per 1.0 g catalyst. This corresponds to 2.0–7.4 molecules of C atom per a surface Ti site.

Table 1. Reaction rate for the benzene photooxidation over metal-loaded TiO_2 catalysts

Catalyst[a]	Reaction rate / 10^{-6} mol min^{-1} g^{-1}
TiO_2	0.81
Rh/TiO_2	2.65
Ir/TiO_2	0.32
Pt/TiO_2	0.75
Pd/TiO_2	1.29

[a]Metal loading, 1 wt%. Benzene, 250 ppm; relative humidity, 50%, reaction temp, 30 °C.

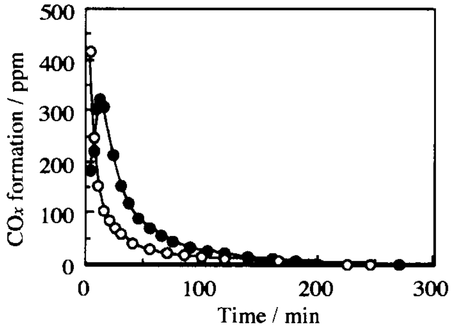

Figure 2. Time course for the CO_x formation in the decomposition of carbon deposits on the used catalysts. (●), TiO_2; (○), Rh/TiO_2; relative humidity, 50% in air; catalyst, 0.24 g.

Figure 2 also shows the formation behavior of CO_x from the carbon deposits on the used Rh/TiO_2. The amount of carbon deposits was estimated to be 134 μmol per 1.0 g catalyst, which was approximately 0.5 times smaller than that for the pure TiO_2. In addition, induction period was not observed for the CO_x formation and the initial rate of the CO_x formation for Rh/TiO_2 was higher than that for TiO_2. These findings imply that deposition of Rh on TiO_2 inhibited the formation of carbon deposits on the catalyst surface and accelerated their decomposition, which improved the catalyst durability of TiO_2 in the benzene photooxidation.

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