Photocatalytic Behavior of WO₃/TiO₂ in Decomposing Volatile Aldehydes

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Removal of volatile organic compounds (VOCs) by photocatalytic treatment has drawn extensive interest as an environmentally-benign technique over the last few decades.¹,² Low molecular weight aldehydes are one of the major VOCs contaminating indoor air.³,⁴ They are usually generated from new architectural ornaments, furniture, merchandize, and plastics, as well as from paint, glue, or other chemicals, and known to be carcinogenic, mutagenic or teratogenic.⁵,⁶ Thus far, photocatalytic decomposition of aldehydes with TiO₂ has been reported by several researchers,⁷⁻¹⁵ but the decomposition characteristics of each aldehyde has not been fully investigated.

Previously, we reported that the monolayer coverage of WO₃ on the surface of TiO₂ particle enhances the photocatalytic activity by 3-4 times in decomposing gaseous 2-propanol or benzene.¹⁶,¹⁷ It was proposed that the major advantage of the WO₃-modified TiO₂ originates from much higher adsorption of organic compound on its surface because of the high Lewis surface acidity of WO₃ covering TiO₂ surface. In the present work, we studied the decomposition trends of the three volatile aldehydes, formaldehyde, acetaldehyde, and propionaldehyde, with the WO₃-modified TiO₂ photocatalyst. Unexpectedly, increase of photocatalytic activity was not observed in decomposing formaldehyde, differently from other aldehydes. We analyzed the surface of formaldehyde-adsorbed photocatalysts to investigate the unusual decomposition behavior of formaldehyde. The obtained result will also provide a new insight to understand the photocatalytic enhancement in the WO₃-modified TiO₂.

The commercial TiO₂, Degussa P25, with a surface area of 50 m²/g, was chosen as a standard. The 3 mol% WO₃/97 mol% TiO₂ (denoted to WO₃/TiO₂; the TiO₂-based composite whose surface is covered with monolayer of WO₃) was prepared by an incipient wetness method. That is, 1.00 g of P25 TiO₂ was suspended in 40 mL of 14.0 M aqueous ammonia solution containing 3.87 × 10⁻⁴ mol of the tungstic acid (99%, Aldrich), and dried in a water bath at 70 °C while stirring. The dried sample was then heat treated at 200 °C for 2 hr in a flowing oxygen.¹⁶,¹⁷

The TEM images in Figure 1 show the pure TiO₂ (Degussa p25) and WO₃/TiO₂ nanoparticles. The uniform lattice fringes observed over an entire particle with the size of about 25 nm indicate that the individual TiO₂ nanoparticle consists of a single grain. The WO₃/TiO₂ nanoparticles also showed the lattice fringes similar to those observed in pure TiO₂, and no WO₃ cluster was found around the TiO₂. This suggests that WO₃ is uniformly dispersed on the surface of TiO₂.

The prepared WO₃/TiO₂ and pure TiO₂ samples were used for the photocatalytic decomposition of each aldehyde in gas phase. For the measurements, an aqueous colloidal suspension containing 2.0 mg of WO₃/TiO₂ or TiO₂ was spread on a 2.5 × 2.5 cm² Pyrex glass, and subsequently dried at room temperature. Then it was located in the center of a 200 mL-sized gas-tight reactor, and the whole area of the sample was irradiated by a 300 W Xe lamp. After evacuation of the reactor, 26 μmol of aldehyde and 170 μmol of water were added to obtain the partial pressures of 2 and 16 Torr, respectively. The total pressure of the reactor was then controlled to 700 Torr by addition of oxygen gas. The gas mixtures in the reactor were magnetically convected during the irradiation. The remained aldehyde and evolved CO₂ during the photocatalytic reaction were monitored by a gas chromatography. The detailed description for the measurement of photocatalytic activity is given elsewhere.¹⁶,¹⁷

Figure 2 shows the photocatalytic removal of the three alkylaldehydes with the WO₃/TiO₂ and pure TiO₂ under a UV light irradiation. The WO₃/TiO₂ was much more effici-

Figure 1. TEM images of TiO₂ (a) and WO₃/TiO₂ (b) nanoparticles. TiO₂ is Degussa P25, and WO₃/TiO₂ denotes to the surface-modified P25 with 3 mol% of WO₃.
ent than the pure TiO$_2$ in decomposing acetaldehyde and propionaldehyde. However, its efficiency was unexpectedly lower than the pure TiO$_2$ in the removal of formaldehyde. Similar trends were also observed in the evolution of CO$_2$, as shown in Figure 3. With TiO$_2$, the amounts of CO$_2$ evolved in 60 min of irradiation were not appreciably different regardless of aldehydes, whereas they were greatly dependent on the kinds of aldehydes when the WO$_3$/TiO$_2$ was applied. That is, in the decomposition of acetaldehyde and propionaldehyde, the amounts of the CO$_2$ evolved in 60 min with the WO$_3$/TiO$_2$ were 2.7 and 1.9 times, respectively, with those with the pure TiO$_2$, whereas the evolved CO$_2$ with the WO$_3$/TiO$_2$ was only 0.75 times in decomposing formaldehyde. Higher photocatalytic activities in decomposing acetaldehyde and propionaldehyde seem to be reasonable, but the lower activity of WO$_3$/TiO$_2$ in the treatment of formaldehyde is an unexpected result.

The amount of the adsorbed formaldehyde on the surface of TiO$_2$ and WO$_3$/TiO$_2$ was determined by thermogravimetric (TG) analysis, as described below. The TiO$_2$ and WO$_3$/TiO$_2$ specimens, pre-dried in vacuum, were kept in a saturated formaldehyde atmosphere at room temperature for 72 hr. Then, the samples were evacuated under about 10 Torr at room temperature for 24 hr to remove the physically adsorbed formaldehyde molecules. The weight increase by the chemically adsorbed formaldehyde on the surface of TiO$_2$ was 0.28%, whereas that of WO$_3$/TiO$_2$ was 1.26%. This indicates that $9.36 \times 10^{-3}$ and $4.25 \times 10^{-4}$ mol/g of formaldehyde were adsorbed on the surfaces of TiO$_2$ and WO$_3$/TiO$_2$, respectively. It is deduced that the great adsorption of formaldehyde originates from the high adsorption affinity of WO$_3$ present on the surface of TiO$_2$, since the Lewis surface acidity of WO$_3$ is about 15 times higher than that of pure TiO$_2$.

The TiO$_2$ covered with monolayer of WO$_3$ can be obtained by the loading 3 mol% of WO$_3$ on the Degussa P25 nanoparticles, and this induces greatly high adsorption affinity toward the organics retaining Lewis basicity.

Figure 4 indicates the IR spectra for the naked and formaldehyde-adsorbed TiO$_2$ and WO$_3$/TiO$_2$, respectively. As shown in Figure 4a and b, there is no appreciable difference in the spectra of the naked TiO$_2$ and WO$_3$/TiO$_2$. The peaks of 3430 and 1640 cm$^{-1}$, shown in all spectra, are from the characteristic vibrations of O-H. In the spectra of the formaldehyde-adsorbed TiO$_2$ and WO$_3$/TiO$_2$, the characteristic organic peaks are clearly shown, as indicated Figure 4c and d. The intensities of those peaks are much higher in the WO$_3$/TiO$_2$ sample than in the naked TiO$_2$. This suggests that more formaldehydes are adsorbed on the surface of WO$_3$/TiO$_2$, and this is compatible with the result determined by TG analysis. As shown in Figure 4c, the vibration peaks at 2913, 1701, 1400, 1225 and 1160 cm$^{-1}$ reveal the presence...
of molecularly adsorbed H₂CO on the surface of TiO₂. By contrast, however, the characteristic peak positions for the WO₃/TiO₂ are shifted or appreciably different from those of TiO₂ (Figure 4d). The peaks of the 2985, 2922, 1385, and 1238 cm⁻¹ are assigned to C-H vibrations, and those of 1120 and 936 cm⁻¹ originates from the asymmetric and symmetric OCO stretching vibrations of (H₂CO)ₙ. In addition, 1095, 1044 and 978 cm⁻¹ peaks represent the CO stretching vibrations. Thus it is clearly indicated from the IR spectra that the paraformaldehyde [(H₂CO)ₙ], a polymerized form of formaldehyde, is present on the WO₃/TiO₂ surface. It is indicated in the literature that formaldehyde is easily polymerized to form a stable paraformaldehyde at its high concentration. We found that the paraformaldehyde was formed on the surface of WO₃/TiO₂ photocatalyst before the photocatalytic decomposition reaction. As determined by TG analysis, 4.5 times of formaldehydes were adsorbed on the surface of WO₃/TiO₂, presumably due to the higher surface acidity of WO₃/TiO₂. Thus the inter-molecular distance of the neighboring formaldehydes will be shorter, and this may induce the polymerization of formaldehyde molecules. The formed paraformaldehyde is relatively difficult to decompose, and this leads to a lower photocatalytic activity of WO₃/TiO₂.

The photocatalytic oxidation reaction was performed in a considerably low formaldehyde concentration, to retard the polymerization of formaldehyde on the catalyst surface. When the initial concentration of formaldehyde was diluted to 1/10 (240 ppm) of the regular concentration (2400 ppm), the evolved amount of CO₂ in 20 min of irradiation with WO₃/TiO₂ was 20% higher than that with the naked TiO₂. Relatively higher efficiency at low formaldehyde concentration suggests that the polymerization of formaldehyde on the catalyst surface is the dominant factor in reducing photocatalytic activity of WO₃/TiO₂.

Formaldehyde is a typical harmful VOC usually released from our daily living environment. In this regards, it has been often used as a standard compound in evaluating the performance of the photocatalysts in decomposing VOCs. As we have demonstrated in this work, however, there is a possibility that it does not offer an appropriate result, since the formaldehyde can be polymerized on the surface of photocatalyst. Especially, with the photocatalysts retaining high adsorption affinity toward organics, formaldehyde may present an abnormal decomposition behavior. Therefore, acetaldehyde or propionaldehyde would be more reasonable choice as a standard compound.

In addition, this experiment provides the clear evidence that the enhanced photocatalytic activity of WO₃/TiO₂ is caused by the excellent adsorption ability of WO₃ covering the surface of TiO₂ by monolayer thickness.

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References