Photocatalytic Behavior of WO_3/TiO_2 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.[1-3] Low molecular weight aldehydes are one of the major VOCs contaminating indoor air.[4,5] 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.[6,7] Thus far, photocatalytic decomposition of aldehydes with TiO_2 has been reported by several researchers,[8-15] but the decomposition characteristics of each aldehyde has not been fully investigated.

Previously, we reported that the monolayer coverage of WO_3 on the surface of TiO_2 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 WO_3-modified TiO_2 originates from much higher adsorption of organic compound on its surface because of the high Lewis surface acidity of WO_3 covering TiO_2 surface. In the present work, we studied the decomposition trends of the three volatile aldehydes, formaldehyde, acetaldehyde, and propionaldehyde, with the WO_3-modified TiO_2 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 WO_3-modified TiO_2.

The commercial TiO_2, Degussa P25, with a surface area of 50 m^2/g, was chosen as a standard. The 3 mol% WO_3/97 mol% TiO_2 (denoted to WO_3/TiO_2; the TiO_2-based composite whose surface is covered with monolayer of WO_3) was prepared by an incipient wetness method. That is, 1.00 g of P25 TiO_2 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 ^oC while stirring. The dried sample was then heat treated at 200 ^oC for 2 hr in a flowing oxygen.[16,17]

The TEM images in Figure 1 show the pure TiO_2 (Degussa p25) and WO_3/TiO_2 nanoparticles. The uniform lattice fringes observed over an entire particle with the size of about 25 nm indicate that the individual TiO_2 nanoparticle consists of a single grain. The WO_3/TiO_2 nanoparticles also showed the lattice fringes similar to those observed in pure TiO_2, and no WO_3 cluster was found around the TiO_2. This suggests that WO_3 is uniformly dispersed on the surface of TiO_2.

The prepared WO_3/TiO_2 and pure TiO_2 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 WO_3/TiO_2 or TiO_2 was spread on a 2.5×2.5 cm^2 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 CO_2 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 WO_3/TiO_2 and pure TiO_2 under a UV light irradiation. The WO_3/TiO_2 was much more effici-

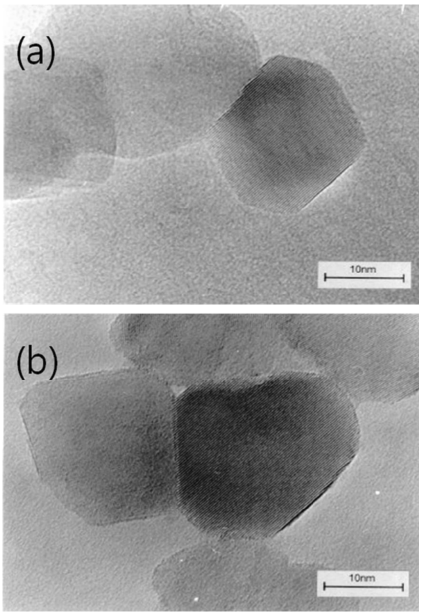

Figure 1. TEM images of TiO_2 (a) and WO_3/TiO_2 (b) nanoparticles. TiO_2 is Degussa P25, and WO_3/TiO_2 denotes to the surface-modified P25 with 3 mol% of WO_3.

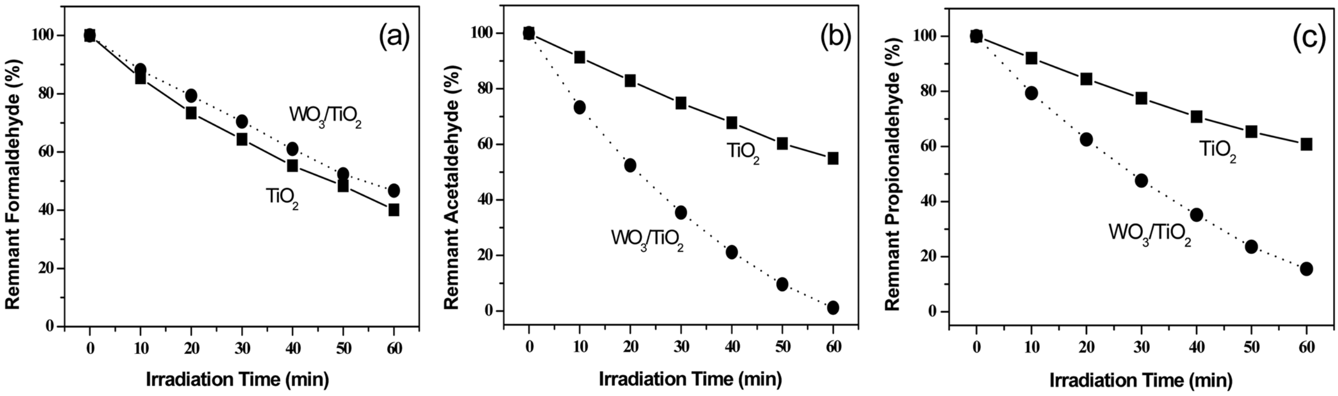

Figure 2. Percentage of remnant formaldehyde (a), acetaldehyde (b), and propionaldehyde (c) as a function of irradiation time by photocatalytic reaction with TiO_2 and WO_3/TiO_2.

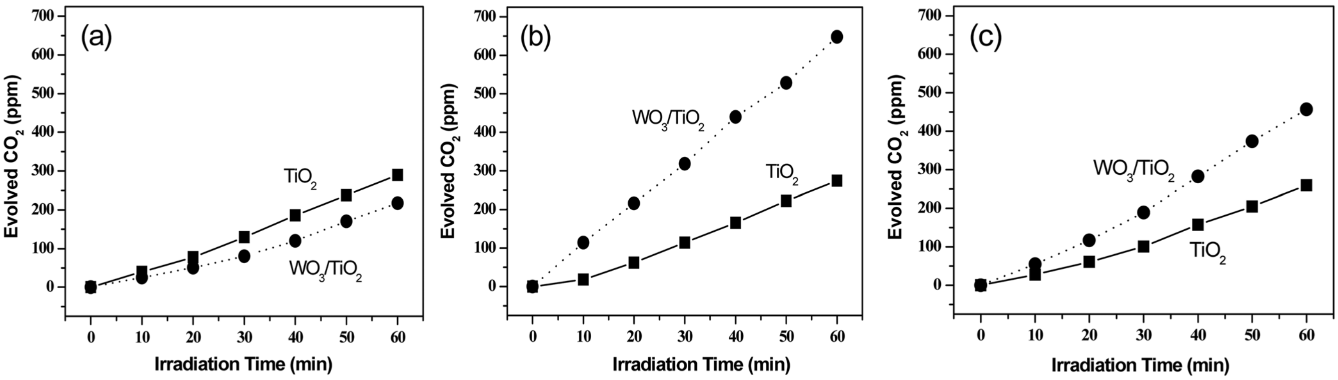

Figure 3. Evolution of CO_2 from formaldehyde (a), acetaldehyde (b), and propionaldehyde (c) as a function of irradiation time with TiO_2 and WO_3/TiO_2 photocatalysts.

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, 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 9.36×10^{-5} and 4.25×10^{-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.[16,17] 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

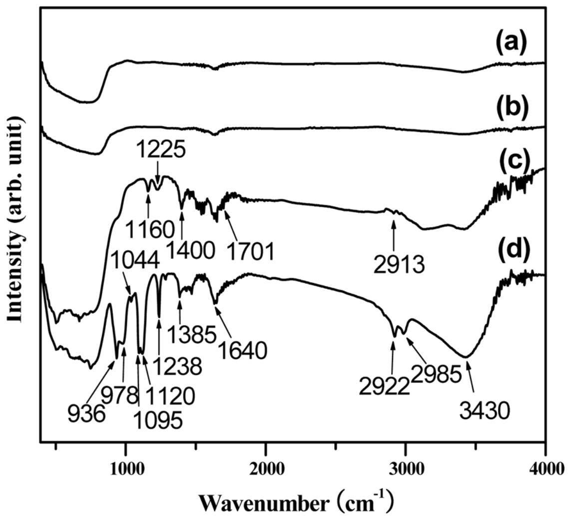

Figure 4. IR spectra of the pure TiO_2 (a) and WO_3/TiO_2 (b), and the formaldehyde-adsorbed TiO_2 (c) and WO_3/TiO_2 (d).

of molecularly adsorbed H_2CO on the surface of TiO_2.[18-22] By contrast, however, the characteristic peak positions for the WO_3/TiO_2 are shifted or appreciably different from those of TiO_2 (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 $(H_2CO)_n$. 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 $[(H_2CO)_n]$, a polymerized form of formaldehydes, is present on the WO_3/TiO_2.[19,20]

It is indicated in the literature that formaldehyde is easily polymerized to form a stable paraformaldehyde at its high concentration.[19,20] We found that the paraformaldehyde was formed on the surface of WO_3/TiO_2 photocatalyst before the photocatalytic decomposition reaction. As determined by TG analysis, 4.5 times of formaldehydes were adsorbed on the surface of WO_3/TiO_2, presumably due to the higher surface acidity of WO_3/TiO_2. 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 WO_3/TiO_2.

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 CO_2 in 20 min of irradiation with WO_3/TiO_2 was 20% higher than that with the naked TiO_2. 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 WO_3/TiO_2.

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 WO_3/TiO_2 is caused by the excellent adsorption ability of WO_3 covering the surface of TiO_2 by monolayer thickness.

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References

1. Inoue, T.; Fujishima, A.; Konishi, S.; Honda, K. *Nature* **1979**, *277*, 637.
2. Chen, M.-L.; Bae, J.-S.; Oh, W.-C. *Bull. Korean Chem. Soc.* **2006**, *27*, 1423.
3. Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W. *Chem. Rev.* **1995**, *95*, 69.
4. Liu, W.; Zhang, J.; Zhang, L.; Turpin, B. J.; Weisel, C. P.; Morandi, M. T.; Stock, T. H.; Colome, S.; Korn, L. R. *Atmos. Environ.* **2006**, *40*, 2202.
5. Brown, S. K. *Indoor Air* **2002**, *12*, 55.
6. O'Brien, P. J.; Siraki, A. G.; Shangari, N. *Crit. Rev. Toxicol.* **2005**, *35*, 609.
7. Marchand, C.; Bulliot, B.; Calve, S. L.; Mirabel, P. *Atmos. Environ.* **2006**, *40*, 1336.
8. Chin, P.; Yang, L. P.; Ollis, D. F. *J. Catal.* **2006**, *237*, 29.
9. Ye, X.; Chen, D.; Gossage, J.; Li, K. *J. Photochem. Photobiol. A: Chem.* **2006**, *183*, 35.
10. Ohno, T.; Tsubota, T.; Kakiuchi, K.; Sayama, K. *Chem. Lett.* **2004**, *33*, 1610.
11. Noguchi, T.; Fujishima, A.; Sawunyama, P.; Hashimoto, K. *Environ. Sci. Technol.* **1998**, *32*, 3831.
12. Fujishima, A.; Rao, T. N.; Tryk, D. A. *J. Photochem. Photobiol. C: Photochem. Rev.* **2000**, *1*, 1.
13. Chen, X.; Mao, S. S. *Chem. Rev.* **2007**, *107*, 2891.
14. Takeda, N.; Torimoto, T.; Sampath, S.; Kuwabata, S.; Yoneyama, H. *J. Phys. Chem.* **1995**, *99*, 9986.
15. Aoki, K.; Morikawa, T.; Ohwaki, T.; Taga, Y. *Chem. Lett.* **2006**, *35*, 616.
16. Kwon, Y. T.; Song, K. Y.; Lee, W. I.; Choi, G. J.; Do, Y. R. *J. Catal.* **2000**, *191*, 192.
17. Song, K. Y.; Park, M. K.; Kwon, Y. T.; Lee, H. W.; Chung, W. J.; Lee, W. I. *Chem. Mater.* **2001**, *13*, 2349.
18. Rasko, J.; Kecskes, T.; Kiss, J. *J. Catal.* **2004**, *226*, 183.
19. Davis, J. L.; Barteau, M. A. *J. Am. Chem. Soc.* **1989**, *111*, 1782.
20. Zamboni, V.; Zerbi, G. *J. Polym. Sci., Part C: Polym. Symp.* **1964**, *7*, 153.
21. Busca, G.; Lamotte, J.; Lavalley, J. C.; Lorenzelli, V. *J. Am. Chem. Soc.* **1987**, *109*, 5197.
22. *The Aldrich Library of FT-IR Spectra*, 1st ed.; Pouchert, C. J., Ed.; Aldrich Chemical Company, Inc.: Milwaukee, Wisconsin, 1985; Vol 1, p 205D.