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The Effect of WO_3 on the Photocatalytic Activity of TiO_2

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Samples of WO_3/TiO_2 mixed oxide powders were prepared by two methods: (1) the incipient wetness impregnation of an aqueous ammonia solution of H_2WO_4 onto TiO_2 (P25), followed by heat treatment and (2) the ultrasonic nebulization and flame hydrolysis of a mixed isopropanol solution of tungsten(V) pentaethoxide and titanium(IV) tetraisopropoxide. The photocatalytic activities of TiO_2-based catalysts were evaluated by the degradation of 1,4-dichlorobenzene (DCB). The addition of WO_3 to TiO_2 greatly increased its photocatalytic behavior. This may be related to an increase in the transfer of electrons from the TiO_2 to the outer system, via the formation of an intermediate W(V) species. © 1994 Academic Press, Inc.

INTRODUCTION

TiO_2 has been shown to be an excellent photocatalyst for the degradation of several environmental contaminants (1,2). Many organic compounds can be oxidized in aqueous solution on the surface of TiO_2 powders illuminated with near-UV or sunlight (3,4).

It has been shown that the photocatalytic activity of TiO_2 is influenced by the crystal structure, surface area, size distribution, porosity, band gap, and surface hydroxyl group density (5–8). Recently, noble metals (Pd, Au, Ag, etc.) deposited on TiO_2 have been widely studied for the purpose of improving the latter's photocatalytic activity (9–13). Gerischer and co-workers (3,11) have proposed that the rate of photooxidation of organic compounds, on the surface of a catalyst, is limited by the rate of electron transfer to oxygen. They have reported that the modification of the TiO_2 surface by noble metals increases the efficiency of electron transfer to oxygen and, hence, increases the efficiency of photoassisted oxidation.

In contrast to metal/TiO_2 photocatalysts, there have been few studies reported concerning the photocatalytic activity of metal oxide/TiO_2 catalysts. Several papers have reported (14,15) on the use of chromium oxide and iron oxide as additives to TiO_2 in order to increase the rate of photooxidation of phenol. Tokumitsu *et al.* (16) have used WO_3/TiO_2 photocatalysts to remove $(CH_3)_3N$, CH_3SH, and CH_3CHO from air. Photooxidation of methanol using a MoO_3/TiO_2 catalyst was reported by Liu *et al.* (17). However, the latter results indicate that the photocatalytic activity was one-fifth that of pure TiO_2.

In this study, it is shown that WO_3/TiO_2 shows a higher photocatalytic activity toward the oxidation of 1,4-dichlorobenzene. The investigation is part of a systematic attempt to prepare mixed oxide systems which can efficiently photodegrade chlorinated hydrocarbons. The choice of WO_3 was based on the relative band position of $WO_3 \cdot xH_2O$ and TiO_2. It has been reported (18,19) that the flat band potential of $WO_3 \cdot xH_2O$ obtained from Schottky–Mott plots is -0.45 V (vs SCE), and that of TiO_2 is -0.7 V. Hence, photogenerated electrons are transferred to the WO_3 conduction band and the holes accumulate in the TiO_2.

Members of the WO_3/TiO_2 system have been reported to act as denitrification catalysts (20,21), and Tennakone *et al.* (19) have suggested that members of the WO_3/TiO_2 system might be more efficient than pure TiO_2 for the photodegradation of water. However, they did not publish experimental data to substantiate their claims. The study reported in this paper is the first which investigates members of the WO_3/TiO_2 system as catalysts for the photooxidation of chlorinated hydrocarbons.

EXPERIMENTAL

Preparation of TiO_2 and WO_3 Powders

A commercial form of TiO_2 (Degussa P25) was chosen as a standard sample of TiO_2. A second sample of TiO_2, studied in this investigation, was prepared by the ultrasonic nebulization and flame hydrolysis of a 0.5 *M* isopropanol solution of titanium(IV) tetraisopropoxide (Johnson Matthey Co.). A solution containing a titanium precursor was nebulized by a commercial ultrasonic humidifier (Holmes Air). The generated mists were carried by argon (flow rate 1.6 liter/min) and fed into the oxy-hydrogen flame (H_2 flow, 3.5 liter/min; O_2 flow, 8.0 liter/min). The TiO_2 powders produced were deposited on the wall of a silica tube. The detailed experimental apparatus has been described in a previous publication (22).

The WO_3 was prepared by the ultrasonic nebulization

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and flame hydrolysis of 0.5 *M* isopropanol solution of tungsten(V) pentaethoxide (Gelest, Inc.). The flame condition was the same as was used for the preparation of the TiO_2 samples.

Preparation of WO_3/TiO_2 and WO_3/Metal Oxide Polycrystalline Samples

Members of the WO_3/TiO_2 system were prepared by the incipient wetness method. An aqueous ammonia solution of H_2WO_4 (Allied Chemical & Dye Corporation, No. 1204), containing 2.0 mg/ml of tungstic acid, was the source of WO_3 in this study. In order to vary the $WO_3 : TiO_2$ content, a fixed weight of TiO_2, P25, as ultrasonically dispersed in varying aliquots of the aqueous ammonia solution of tungstic acid. Each solution was then evaporated in a water bath. The product was subsequently dried in a drying oven at 120°C for 16 hr and ground with a mortar and pestle. Finally, the product was calcined in an oxygen gas stream (100 cm^3/min) at 450°C for 1 hr.

In addition, WO_3/TiO_2 samples were prepared by the ultrasonic nebulization and flame hydrolysis of a 0.5 *M* mixed isopropanol solution of tungsten(V) pentaethoxide and titanium(IV) tetraisopropoxide. The flame condition was the same as was used for the preparation of TiO_2.

WO_3 was also added to other binary metal oxide supports, such as SiO_2, SnO_2, Al_2O_3, and ZrO_2 by the incipient wetness impregnation of an aqueous ammonia solution of H_2WO_4. The preparation condition was the same as was used for the preparation of samples of WO_3/TiO_2.

Characterization of Products

X-ray powder diffraction patterns of the powder samples were obtained using a Philips diffractometer and monochromated high intensity Cu$K\alpha_1$ radiation (λ = 1.5405 Å). The diffraction patterns were taken with a scan rate of 1° 2θ min^{-1} over the range $12° < 2\theta < 80°$, while cell parameters were determined from scans taken at 0.25° 2θ/min. Precise lattice parameters were obtained from the diffraction peaks using a least-squares refinement program which corrects for the systematic errors of the diffractometer.

Crystallite sizes were calculated from the peak widths by using the Scherrer equation, $D = k\lambda/(\beta \cos \theta)$, where D is the crystallite size, k is a shape factor (a value of 0.9 was used in this study), λ is the X-ray radiation wavelength (1.5405 Å for Cu$K\alpha_1$), and β is the half width (in radians) of the peak at 2θ. β was determined from the experimental integral width by applying standard corrections for the effects of $K\alpha_1$–$K\alpha_2$ separation and instrumental broadening.

The surface area was measured by the single-point BET method using a Flow Sorb (II) 2300 (Micromeritics Instrument Corp., Norcross, GA). The samples were degassed at 170°C for 2 hr and the adsorbate gas consisted of a mixture of 30% N_2/70% He.

Measurement of Photocatalytic Activity

The photocatalytic activities of various powder samples were evaluated by the degradation of 1,4-dichlorobenzene (DCB). A saturated DCB solution was prepared by adding an excess of DCB to distilled water and stirring for 8 hr. The solution was capped and preserved in darkness. A standard stock solution containing 0.0015 wt% of the ultrasonically dispersed oxide was prepared. Three ml of this solution was transferred to a silica cuvette and 0.2 ml of a saturated aqueous solution of DCB was added. A sample containing 0.2 ml of distilled water and 3 ml of the TiO_2 suspension was used as a blank for the absorption measurement. The sample was then irradiated with a 150-watt xenon short-arc lamp whose output was passed through a pyrex filter. The differential absorption at 224 nm (maximum absorption peak of DCB) was measured using a Perkin–Elmer 552A spectrophotometer. The change in concentration of DCB of the irradiated sample as a function of time was compared to that of the blank.

RESULTS AND DISCUSSION

There have been relatively few phase studies carried out on the WO_3/TiO_2 system. Several techniques were used to obtain information concerning the surface structure of members of the WO_3/TiO_2 system. They included Raman spectroscopy, X-ray diffraction spectroscopy (XRD), X-ray absorption spectroscopy (XANES), and Fourier transformation infrared spectroscopy (FTIR) (23–28). These studies have revealed that impregnated WO_3 clusters on the surface of the TiO_2. Ramis *et al.* reported (26) that the WO_3 surface consists of wolframyl groups (W = O) and the WO_3 inhibits the phase transformation of anatase to rutile. In this study, the cell parameters of two WO_3/TiO_2 samples are compared to those observed for TiO_2 (P25) and TiO_2 prepared by flame hydrolysis of titanium(IV) tetraisopropoxide (Table 1). There appears to be no detectable change in cell parameters, which limits the degree of solid solution of WO_3 in TiO_2 to less than 2 mole%. Table 1 also shows little difference in the surface area and crystallite size of the prepared WO_3/TiO_2 powders and pure TiO_2 samples.

The photocatalytic activity of WO_3/TiO_2 powder samples was evaluated by the degradation of 1,4-dichlorobenzene (DCB). Samples were irradiated for 10 min with a xenon lamp. Figure 1 shows the change in concentration of DCB as a function of irradiation time. It can be seen that pure WO_3 shows little catalytic activity compared to TiO_2. Samples of TiO_2 prepared by flame hydrolysis of titanium(IV) tetraisopropoxide were not as active as P25. This is consistent with the lower surface area and larger

TABLE 1
Structural Data for TiO_2 and WO_3/TiO_2 (mole% 10/90) Samples

Sample	Preparation	Calcination temperature (°C)	Surface area (m^2/g)	Crystallite[a] size (nm)	X-ray I_{max} anatase/rutile	Cell parameter (Å) of TiO_2[b]
TiO_2	P25 Degussa	R.T.	47	17	71/29	a = 3.781(2) c = 9.490(2)
TiO_2	Flame hydrolysis	As prepared	34	26	99/1	a = 3.780(2) c = 9.491(2)
WO_3/TiO_2 (mole% 10/90)	Incipient wetness	450[c]	49	18	70/30	a = 3.781(2) c = 9.488(2)
WO_3/TiO_2 (mole% 10/90)	Flame hydrolysis	As prepared	30	25	99/1	a = 3.783(2) c = 9.491(2)

[a] Crystallite size of anatase phase of TiO_2.
[b] Cell parameters of anatase phase of TiO_2.
[c] WO_3/TiO_2 samples prepared at 450°C gave optimum photocatalysts.

crystallite size of the particles formed by flame hydrolysis of the alkoxide. The two WO_3/TiO_2 samples show approximately a 100% increase in photocatalytic activity over a pure TiO_2 sample which has been heated to 450°C. The optimum loading of WO_3 on TiO_2 (P25) particles was determined by measuring the activity of various WO_3/TiO_2 samples. The results of these measurements are plotted in Fig. 2. It can be seen that the optimum concentration of WO_3 on TiO_2 powders is 3 mole%.

The fundamental process which occurs in TiO_2 photocatalysts requires the promotion by light excitation of a valence band electron to the conduction band. In the presence of WO_3, these electrons can be transferred to WO_3, resulting in the formation of W(V) species.[1] This would be consistent with the results of Tennakone *et al.* (19), which reported that when WO_3 particles in contact with TiO_2 in water are irradiated with light, there is an electron transfer from TiO_2 to $WO_3 \cdot xH_2O$. However, the

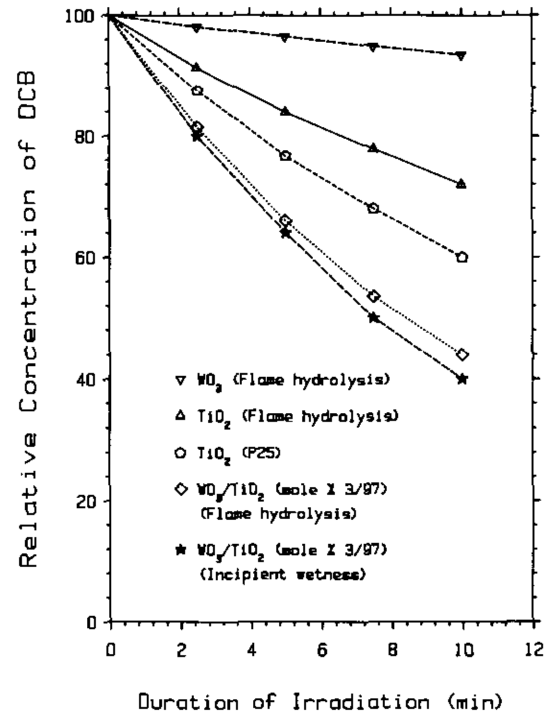

FIG. 1. Decomposition of DCB vs irradiation time of TiO_2, WO_3, and WO_3/TiO_2 powders.

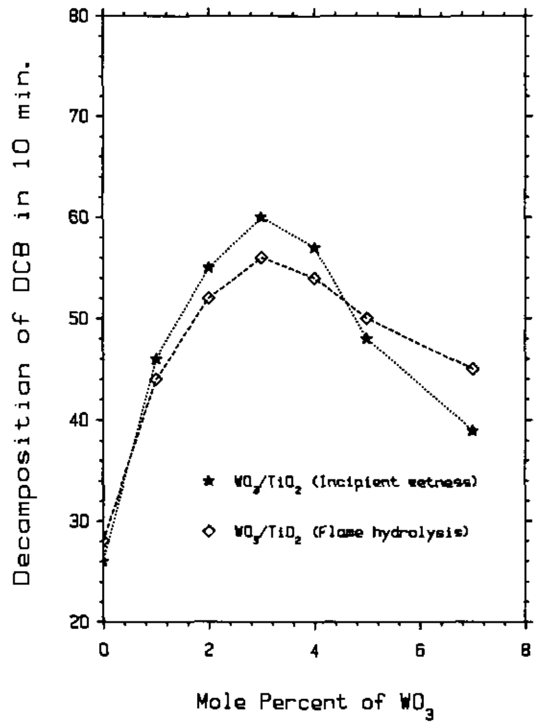

FIG. 2. Photocatalytic activity of TiO_2 powders as a function of concentration of WO_3.

TABLE 2
Photocatalytic Activity of 3 mole% WO_3 over Various Supporting Oxides

Supporting oxide	TiO_2 (P25)	SiO_2	SnO_2	Al_2O_3	ZrO_2
Photocatalytic activity[a]	60	1	2	2	2

[a] % of DCB decomposition in the initial 10 min of irradiation.

lack of a blue color due to the W(V)–W(VI) couple is undoubtedly related to the ease by which the electron from tungsten can be transferred to the outer systems (air). This electron-hole separation process then permits the separated holes to transfer to OH^-, creating the active oxidant OH^*. The dispersed WO_3 particles play an important role in accepting the photogenerated electrons from TiO_2, and these electrons are transferred to oxygen adsorbed on the surface of the TiO_2 particles. The increased photocatalytic activities shown by the WO_3/TiO_2 samples are consistent with the model of Gerischer and Heller (3), which predicted increased activity of the photocatalyst if the electron transfer rate-controlling step could be made more efficient.

In order to test if WO_3 itself is photocatalytically active or if it only modifies the support, WO_3 was introduced onto several supports. Colloidal particles of SiO_2, SnO_2, Al_2O_3, and ZrO_2, which have high surface areas, can readily be dispersed in an aqueous solution. A 3 mole% of WO_3 was introduced on these supporting materials by the same incipient wetness technique which was used for the preparation of the WO_3/TiO_2 samples. Table 2 shows that WO_3 supported over SiO_2, SnO_2, Al_2O_3, or ZrO_2 shows low activity. Therefore, WO_3 in the presence of supports which show little photocatalytic activity remains inactive.

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