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Comparative Studies on the Deactivation and Regeneration of TiO_2 Nanoparticles in Three Photocatalytic Oxidation Systems: C_7H_{16}, SO_2, and C_7H_{16}–SO_2

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Three photocatalytic oxidation (PCO) systems: C_7H_{16}–O_2, SO_2–O_2 and C_7H_{16}–SO_2–O_2 were carried out with the aid of UV-illuminated TiO_2 nanoparticles at room temperature in a batch reactor. In C_7H_{16}–O_2–TiO_2 system, no catalyst deactivation was observed, while for SO_2–O_2–TiO_2 and C_7H_{16}–SO_2–O_2–TiO_2 systems, the photocatalytic activity of used TiO_2 powder showed decreasing and eventually no activity after used consecutively. The reaction products such as sulfur trioxide or sulfuric acid adsorbed onto the surface of TiO_2 catalyst were poisoning species. Photocatalytic activity of the deactivated TiO_2 powder could be regenerated by sonicating treatment with water and methanol for the two systems, respectively. © 2002 Elsevier Science (USA)

Key Words: **deactivation; regeneration; TiO_2; heptane; sulfur dioxide.**

1. INTRODUCTION

Heptane and sulfur dioxide are two most important organic and inorganic contaminants in the air, respectively. Moreover, the homogeneous photoreaction between the two compounds can induce photochemical smog (1). TiO_2 photocatalytic oxidation (PCO) is a very effective way to destroy a large variety of organic and inorganic pollutants (2, 3). Its photocatalytic detoxification of compounds is generally more efficient in the gas phase than in the liquid phase (4). Thus, we aimed at the heterogeneous PCO destruction of heptane, SO_2 or both in recent years (5, 6). In this paper, the deactivation and regeneration mechanism of TiO_2 photocatalysts for the three systems: C_7H_{16}–O_2–TiO_2, SO_2–O_2–TiO_2 and C_7H_{16}–SO_2–O_2–TiO_2 are emphasized.

Although TiO_2 has been proven to be very active in the photooxidation of different organic compounds, deactivation has been already reported (7–9). It was suggested that strongly adsorbed species were responsible for the deactivation, and that regeneration method could be a function of the type of the adsorbed species (10–12). Peral and Ollis (13) studied TiO_2 PCO of decamethyltetrasiloxane, indole, pyrrole, and dimethyl sulfide, and observed both reversible and irreversible deactivation depending on the organic compound. None of the batch reactor studies reported catalyst deactivation. This result is plausible, as the changing concentrations characteristic of batch operation could mask any relatively slower catalyst deactivation. As pointed out by Sauer and Ollis (14), deactivation would only be clearly evident if repeat runs were made without catalyst pretreatment or regeneration between runs. To the best of our knowledge, such repeat run data are not reported in the gas–solid PCO system. The present work first initiated examination of photocatalyst deactivation driven by photocatalytic oxidation of SO_2 and C_7H_{16}–SO_2 in a batch reactor. Infrared spectroscopy (IR) and X-ray photoelectron spectroscopy (XPS) analyses were used to identify surface species formed in the C_7H_{16}–SO_2–O_2–TiO_2 system. Gas chromatography–mass spectrometry (GC–MS) analysis of methanol-extracted surface species from the deactivated catalysts was used to confirm the formation of those species.

2. EXPERIMENTAL

The catalyst used was TiO_2 nanoparticles prepared by colloidal chemical method (15). The particle obtained was calcinated at 673 K. X-ray analysis (D/Max-ãA powder diffractometer with nickel-filtered Cu*Kα* source) of the TiO_2 particle revealed the presence primarily of anatase and the mean crystallite size was estimated to be 12 nm using the Scherrer equation (16). The specific surface area

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of the TiO_2 particle was $40.5\,m^2\,g^{-1}$, as determined by the BET method (Micromeritics ASAP 2010).

In a typical experiment, 0.1 g of TiO_2 powder was spread uniformly over the internal surface of a 300 mL quartz batch reactor. After that, 0.4% (v/v, i.e., 166 μM) heptane (or 0.4% sulfur dioxide, or 0.4% heptane and 0.4% sulfur dioxide, depending upon different systems) and 20% oxygen (v/v) were injected into the vacuum-packed reactor with ultrapurity nitrogen as balanced gas to reach one atmospheric pressure. After adsorption equilibrium was reached, as measured by GC, the reaction was started by turning on the 400 W high-pressure mercury lamp. The primary wavelength distribution of this lamp is at 365 nm and the light intensity is $5.3\,mW\,cm^{-2}$ at 15 cm away from the lamp. Subsequently, the amount of heptane was measured every 30 min by a Varian 3700 GC equipped with a flame ionization detector and a SE-54 quart capillary column at 323 K. The measurement of sulfur dioxide was performed every 30 min by a GC equipped with a thermal conductivity detector and a GDX-102 stainless-steel column at 373 K. It was found that for SO_2–O_2–TiO_2 and C_7H_{16}–SO_2–O_2–TiO_2 systems, the TiO_2 catalyst activity decreased for each run when the same catalyst was used on consecutive runs. The repetitions were continued until the catalysts were completely deactivated, as compared with the homogeneous photoreaction rates. In the SO_2–O_2–TiO_2 system, the gas in the reactor was carried by ultrapure nitrogen through $0.1\,mol\,L^{-1}$ $BaCl_2$ solution after each run. The white precipitate that was insoluble in HCl solution indicated that there was sulfur trioxide in the gas phase. Liquid sulfur trioxide was analyzed by the same principle after the catalyst was completely deactivated. The deactivated catalyst was extracted by sonicating with water. The resulting TiO_2 powder was used again to examine whether its photocatalytic activity was recovered or not. In the C_7H_{16}–SO_2–O_2–TiO_2 system, the completely deactivated catalyst, which revealed a change in color from white to yellow, was washed by sonicating in methanol. The resulting solution was examined by GC–MS (HP 6890 GC/HP 5973 MS) with an HP-5MS column (30 m × 0.25 mm). The resulting TiO_2 powder, which restored the original color, was also used again to examine whether its photocatalytic activity was restored or not.

The structure and properties of fresh and deactivated TiO_2 particles (hereafter abbreviated as T_f and T_d, respectively) in C_7H_{16}–SO_2–O_2–TiO_2 system were studied by means of IR and XPS. IR patterns were acquired from a Nicolet Impact 410 infrared spectrophotometer; XPS data were taken from a VG · ESCALAB MK II photoelectron spectrometer. The X-ray source emitted Al$K\alpha$ radiation (1436.8 eV). For all the spectra obtained, pressure was maintained at 6.3×10^{-5} Pa. Binding energies were calibrated with respect to the signal for adventitious carbon (binding energy = 284.6 eV).

3. RESULTS AND DISCUSSION

3.1. The Photocatalytic Activity of TiO_2 in C_7H_{16}–O_2–TiO_2 System

In the condition that both UV light with suitable energy and oxygen are available, reactive oxygen species such as O_2^-, O^-, O, $\cdot OH$ and $HO_2\cdot$ were generated on the surface of TiO_2 (11, 17, 18). Both holes and reactive oxygen species such as $\cdot OH$ have been proposed as the species responsible for initiating the oxidative attack on organic compounds. As for the C_7H_{16}–O_2–TiO_2 system, the PCO of heptane did not proceed in the absence of either TiO_2 or UV light irradiation. However, once there was both TiO_2 and UV light irradiation, C_7H_{16} could be completely photooxidized by the aid of the above species, producing stoichiometrical CO_2 and H_2O (5). When the same TiO_2 catalyst was used consecutively over 100 runs (i.e., over 200 h), its photoactivity was still the same as that of the fresh one, i.e., the photoactivity of TiO_2 could be sustained indefinitely. Consequently, the IR and XPS spectra of the used TiO_2 were the same as that of the fresh one. It has been reported by others that the catalytic activity of TiO_2 could be maintained indefinitely under an abundance of water vapor (11,12,19–21). It was well established that UV illumination of hydroxylated titania in the presence of gaseous O_2 produced surface hydroxyl radicals. Infrared spectroscopy studies (22) during TCE oxidation showed that the titania surface became partially dehydroxylyzed as the reaction proceeded. If hydroxyl radicals were consumed in the heterogeneous oxidation reactions, then the surface must be continuously rehydrated if long-term catalytic activity was to be maintained. Since heptane could be photooxidized quickly to the final products CO_2 and H_2O (5), the surface of TiO_2 was clean after each run of photoreaction. In addition, although hydroxyl radicals may sustain continuous consumption during photocatalysis, water formed as a product of the reaction may replenish the consumed hydroxyl radicals through rehydration to maintain photocatalyst activity.

3.2. The Photocatalytic Activity of TiO_2 in SO_2–O_2–TiO_2 System

As for the SO_2–O_2–TiO_2 system, the PCO of SO_2 did not proceed in the absence of UV light irradiation. The homogeneous photooxidation of SO_2 without TiO_2 can occur. It is known that upon irradiation, SO_2 molecules produce singlet state ($^1SO_2$) and triplet state ($^3SO_2$) species, and $^3SO_2$ is often believed to be the predominant species in the photochemical reaction of sulfur dioxide (23). Both homogeneous and heterogeneous photooxidation reactions of SO_2 fit pseudo-first kinetics. The kinetics equation is $\ln c_0/c = k_a t$, where k_a is the apparent rate constant, c_0 is the initial concentration, and *c* is the concentration at illumination time *t*. Table 1 lists the reaction rate constants including the cases without and with fresh, deactivated and regenerated TiO_2 catalysts. From Table 1, we can see that the photodegradation rate of SO_2 can be accelerated in the presence of fresh TiO_2 powder. Figure 1 shows the variations of rate constants k_a with run number. From Fig. 1(a), we can see that when the same TiO_2 was used consecutively, its activity decreased for each run until it lost activity totally at the twenties run. At this time, the reaction rate was very close to the one when there was no TiO_2, as shown in Table 1. The qualitative analysis results showed that sulfur trioxide in the gas phase was about 3.0% of the theoretical value, and sulfur trioxide in the form of liquid was about 92.3%. So it was inferred that the PCO product of sulfur dioxide was sulfur trioxide, which accumulated on the surface of TiO_2 catalyst and made the catalytic activity disappear gradually. The deactivated TiO_2 was treated by sonicating in water to get the regenerated TiO_2. From Table 1, we can see that the activity was recovered, indicating that adsorbed SO_3 was deleted by water from TiO_2 surface. SO_3 is the species responsible for the deactivation of TiO_2 catalyst.

3.3. The Photocatalytic Activity of TiO_2 in C_7H_{16}–SO_2–O_2–TiO_2 System

In the C_7H_{16}–SO_2–O_2–TiO_2 system, there was not only the homogeneous photochemical reaction between C_7H_{16} and SO_2, but also the heterogeneous photocatalytic reaction of C_7H_{16} and SO_2 on TiO_2 surface. The reaction of C_7H_{16} and SO_2 with or without TiO_2 fits pseudo-first kinetics, with rate constants shown in Table 1. Photochemical reaction mechanism of sulfur dioxide with alkanes can be considered as a chain reaction induced by radicals (1). When TiO_2 was introduced, the photoreaction of sulfur dioxide with heptane was promoted by the aid of reactive oxygen species. From Figs. 1b and 1c, we can see that the rate constants of C_7H_{16} and SO_2 decreased with increased run number. After the same TiO_2 was used for the fourth run, the rate constant was consistent with the one when there was no TiO_2 catalyst existing, indicating that the catalyst was deactivated totally.

TABLE 1

The Reaction Rate Constant k_a (min^{-1}) of Reactants in SO_2–O_2–TiO_2 and C_7H_{16}–SO_2–O_2–TiO_2 Systems without and with Fresh, Deactivated, and Regenerated TiO_2

		Rate constants k_a (min^{-1})		
		SO_2–O_2–TiO_2 system	C_7H_{16}–SO_2–O_2–TiO_2 system	
Samples		SO_2	C_7H_{16}	SO_2
Without TiO_2		5.3×10^{-3}	2.1×10^{-3}	6.6×10^{-3}
	Fresh	2.8×10^{-2}	7.6×10^{-3}	2.1×10^{-2}
With TiO_2	Deactivated	5.2×10^{-3}	2.0×10^{-3}	6.7×10^{-3}
	Regenerated	2.8×10^{-2}	7.7×10^{-3}	2.0×10^{-2}

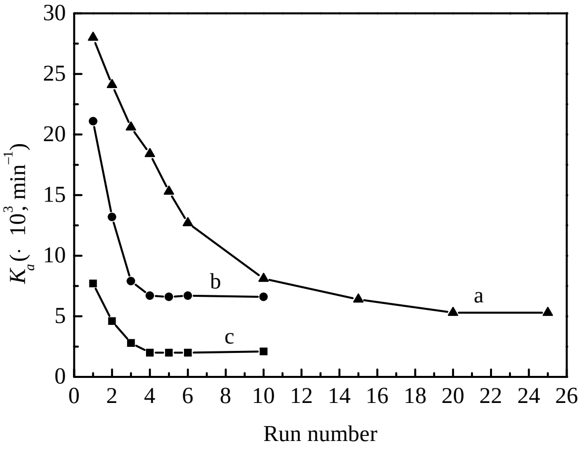

FIG. 1. The variations of rate constants for different reactants with run number. (a) SO_2 in SO_2–O_2–TiO_2 system; (b) SO_2 in C_7H_{16}–SO_2–O_2–TiO_2 system; (c) C_7H_{16} in C_7H_{16}–SO_2–O_2–TiO_2 system.

3.3.1. The Characterization of T_f and T_d. The infrared spectra of T_f and T_d are shown in Fig. 2. From Fig. 2, we could see that there were three new peaks at the position of 1717.91, 1222.65 and 1049.09 cm^{-1} of T_d which could be assigned to C=O, C–O and SO_4^{2-}, respectively (22).

Figure 3 shows the XPS survey spectra for the surface of T_f and T_d. It could be seen from Fig. 3 that T_f and T_d contained Ti, O, S and C elements. It should be noted that element S on T_f was due to the original material $Ti(SO_4)_2$. The amounts of Ti (5.5%) and O (49.4%) of T_d

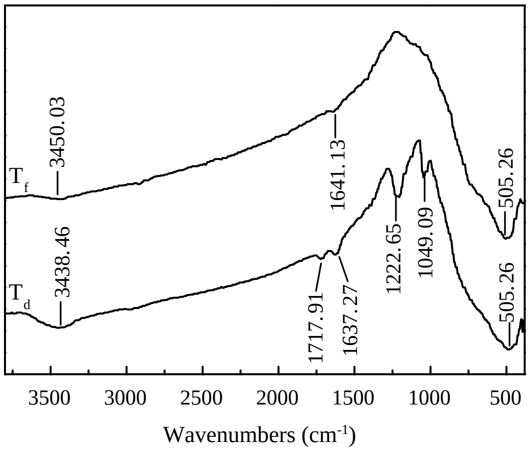

FIG. 2. IR spectra of T_f and T_d samples.

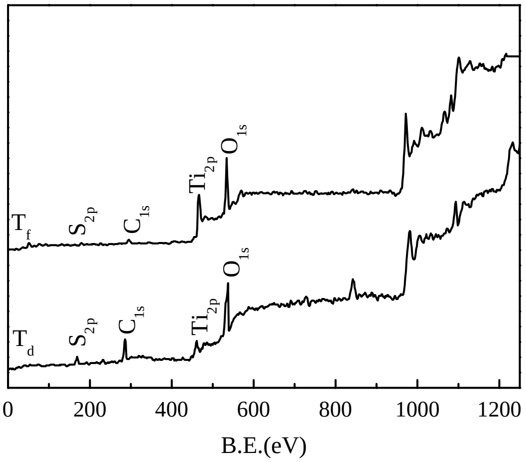

FIG. 3. XPS survey spectra for the surface of T_f and T_d samples.

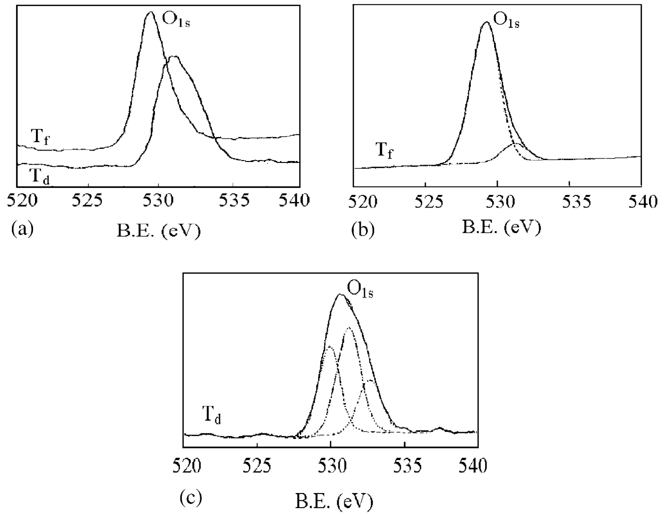

FIG. 4. XPS spectra of the O_{1s} region of T_f and T_d samples (a), the corresponding high-resolution spectra of T_f (b) and T_d (c), respectively.

were lower than those of T_f (Ti: 23.3%, O: 63.8%), while the amounts of S (11.4%) and C (33.7%) of T_d were higher than those of T_f (S: 3.1%, C: 9.8%). So it was inferred that the surface of T_d was covered by substrates containing elements C and S. The O_{1s} binding energy of T_d is 2.0 eV higher than that of T_f (as shown in Fig. 4a). Figs. 4b and 4c show the high-resolution XPS spectra of O_{1s} region, taken on the surface of T_f and T_d. According to Sanchez (24), in the order of increasing binding energy, the three deconvoluted signals of O_{1s} peak could be assigned to lattice oxygen ions O^{2-} (about 529.8 eV), to OH group (about 531.8 eV), and to adsorbed oxygen-containing species (about 533.1 eV). From deconvoluted results, we could see that for T_f, O_{1s} peak was due to the contribution of lattice oxygen (83.40%) and OH group (16.59%), and there were almost no oxygen-containing species adsorbed on the surface of T_f. While for T_d, O_{1s} peak contained lattice oxygen (34.83%), OH group (46.03%) and oxygen-containing species (19.13%). The increased amount of OH group and oxygen-containing species might be due to the reaction products adsorbed onto T_d, which covered the lattice oxygen and made its amount to decrease.

3.3.2. The GC–MS analysis of products on T_d. The decrease in rate constants with runs most likely indicates that byproducts are adsorbing on the catalyst surface and causing it to deactivate. Moreover, the color change of used catalysts in the C_7H_{16}–SO_2–O_2–TiO_2 system is directly associated with the accumulation of those intermediates on the surface. The identification of surface-adsorbed species accumulated on deactivated TiO_2 surface was carried out by the GC–MS analysis, by extraction with methanol. Several stable products, 2-butenoic acid, 2-hydroxyl-propanoic acid, 3-hydroxyl-butanoic acid, 3-heptanone, 4-heptanone, heptoic acid and sulfuric acid, were identified on the deactivated TiO_2 surface. It should be noted that these organic byproducts form surface poisons faster than they can be oxidized photocatalytically. The GC–MS analysis gave evidence to IR and XPS results. The electron withdrawing groups such as carboxide and sulfate present in the above organic acids and sulfuric acid made the binding energy of O_{1s} to increase.

The regenerated catalyst, got by sonicating in methanol, presented nearly the same rate constants for both C_7H_{16} and SO_2 as the fresh TiO_2, as shown in Table 1. It is indicated that the adsorbed poisoning species have already been washed. This is a further evidence that strongly adsorbed species are responsible for the observed catalytic deactivation.

4. CONCLUSION

(1) In the C_7H_{16}–O_2–TiO_2 system, photocatalytic activity of TiO_2 can sustain for a long time. This is because the used TiO_2 can keep clean and also the consumed hydroxyl radicals can be replenished by the produced water.

(2) It is indicated that the adsorbed products block the active sites of TiO_2 and make its photocatalytic activity disappear. In the SO_2–O_2–TiO_2 system, SO_3 was the poisoning species. In the C_7H_{16}–SO_2–O_2–TiO_2 system, inorganic species such as sulfuric acid, as well as many other identified organic byproducts recalcitrant to the photocatalytic process, participate in the loss of catalyst activity.

(3) When the adsorbed products were removed by sonicating in water or methanol, the deactivated catalyst was regenerated.

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