JOURNAL OF CATALYSIS **158,** 97–101 (1996)
ARTICLE NO. 0010

Photocatalytic Degradation of 1-Octanol on Anchored Titanium Oxide and on TiO_2 Powder Catalysts

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Received February 22, 1995; revised August 22, 1995; accepted August 29, 1995

The liquid-phase photocatalytic oxidative degradation of 1-octanol in oxygenated acetonitrile on highly dispersed titanium oxide catalysts anchored onto transparent Vycor glass was compared with that obtained on standard TiO_2 powder. The anchored photocatalysts were prepared through the facile reaction between surface OH groups of Vycor glass and $TiCl_4$. UV irradiation of the anchored catalyst at room temperature led to the photocatalytic degradation of 1-octanol and the production of 1-octanal as the major product. The large surface area of the photocatalyst was one of the most important factors in achieving a high efficiency in the liquid-phase photocatalytic reaction. The specific photocatalytic activity per unit weight of titanium oxide of the highly dispersed anchored catalyst was much higher than that for the TiO_2 powder because of the high activity of the charge transfer complex $(Ti^{3+}–O^{-})^*$. Furthermore, the filtration of the anchored photocatalysts from the liquid reactants was much easier than that of the small particles of TiO_2 powder.

INTRODUCTION

The use of photon energy to induce effective chemical redox reactions can be achieved by photocatalytic and/or photo-electrochemical activation of light-sensitive semiconductor surfaces. Heterogeneous photocatalysis on small TiO_2 particles suspended in an aerated liquid solution containing oxidizable substrates has been employed as a method for the oxidative degradation of toxic compounds, for solar energy conversion, and for selective chemical synthesis (1–6). Although the utilization of extremely small TiO_2 particles as photocatalysts has attracted a great deal of attention (7, 8) especially for environmental applications (9, 10), the actual factors that control the photocatalytic activity of specific TiO_2 particles are still unknown. The catalytic effectiveness of small semiconductors can vary greatly with the physical properties of the sample (11). In addition, in practical applicatons, the separaton of the TiO_2 particles from the contaminated solution constitutes a major difficulty.

Photoresponsive semiconductors included on or inside inert supports offer several possible advantages over native photocatalysts (12, 13). Although composite photocatalysts prepared by an anchoring method are promising as practical and efficient catalysts for gas-phase detoxification (14, 15), the photocatalytic properties of these samples have not yet been clarified for the liquid-phase reactions. In this study, liquid-phase photocatalytic degradation of 1-octanol by titanium oxide anchored on Vycor glass was compared with that obtained on small particle TiO_2 powders.

EXPERIMENTAL

Catalyst. Titanium oxide anchored onto Vycor glass (Ti/VG) was prepared, as shown in Scheme 1, by the reaction of $TiCl_4$ with the surface OH groups of a transparent porous Vycor glass (Corning code 7930, BET surface area 150 m^2g^{-1}) in the gas phase at 473 K, followed by treatment with H_2O vapor to hydrolyze the anchored compounds (Ti/VG-1) (15). The anchoring procedures were repeated three to five times to increase the number of surface layers of the anchored titanium oxide on the Vycor glass (Ti/VG-3 and Ti/VG-5). The resulting Ti/VG samples were calcined at 773 K under O_2 and pulverized before use. The titanium content of the anchored catalysts were Ti/VG-1, 0.17; Ti/VG-3, 0.94; and Ti/VG-5, 1.6 wt%, respectively. A significant change in the surface area of the sample was not observed after these anchoring procedures.

Absorption spectra of the Ti/VG catalysts were recorded with a Shimazu UV-2200A spectrometer operated in the diffraction mode at room temperature. The photoluminescence spectra of the Ti/VG catalysts were recorded at 77 K with a Shimazu RF-501 spectrofluorometer equipped with filters to eliminate scattered light. XAFS spectra (XANES and EXAFS) were obtained at the BL-7C facility of the Photon Factory at the National Laboratory for High-

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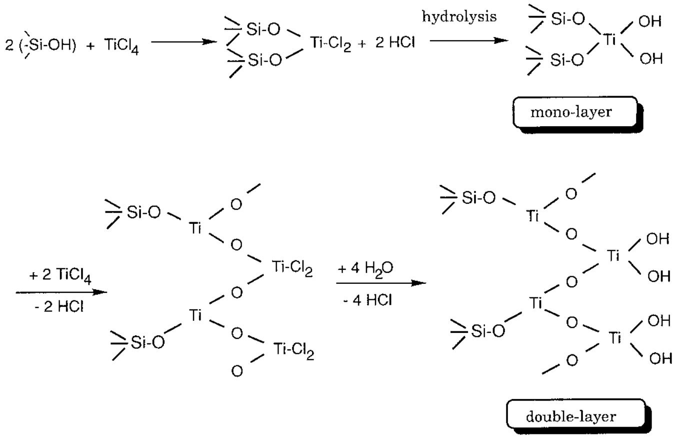

SCHEME 1. Representation of the anchoring procedures.

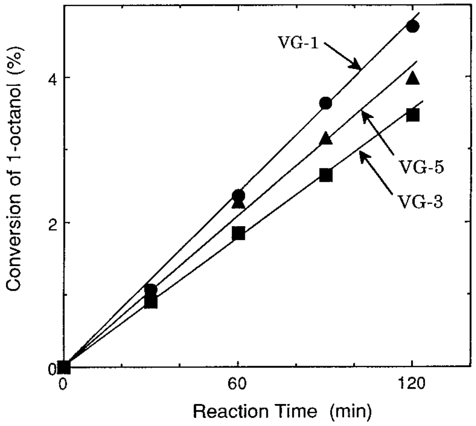

FIG. 1. Reaction profile for the photocatalytic degradation of 1-octanol over titanium oxide anchored on Vycor glass under irradiation at around 300 nm.

Energy Physics, Tsukuba. Si(111) double crystals were used to monochromatize the X-rays from the 2.5-GeV electron storage ring. The Ti K-edge absorption spectra were recorded in the fluorescence mode for the anchored catalysts or in transmission mode for the TiO_2 powder at 295 K. Fourier transformation was performed on k^3-weighted EXAFS oscillations in the range 3–10 $Å^{-1}$.

Five different types of "standard TiO_2 catalysts" (JRC-TIO-1, 2, 3, 4, 5) supplied by the Catalysis Society of Japan were used as powders (grain size, 0.02–1 mm). Detailed information on these standard TiO_2 catalysts (16) is available from the Society. The typical physical properties of these TIO-1–5 catalysts are shown in Table 1. The relative –OH concentration was calculated from the intensities of the IR peak of samples assigned to the surface OH group on TiO_2. The acid concentration was calculated from the peak intensities observed in the temperature-programmed desorption (TPD) patterns of preadsorbed NH_3.

Photocatalytic degradation of 1-octanol. The catalyst (JRC, 25 mg; Ti/VG, 50 mg) was preheated in dry air at 673 K and cooled to room temperature before being placed with 1-octanol (0.5 mmol) in a volumetric flask (25 ml) which was then filled with acetonitrile. The resulting mixture was sonicated for 20 min to suspend the catalyst. The sample was then transferred to a quartz test tube (30 mm i.d.) and sealed with a rubber septum. Oxygen was bubbled through a Teflon tube (1 mm i.d.) and the sample was irradiated at 300 K with vigorous and continuous stirring in a Rayonet Photochemical Reactor (Southern New England Ultraviolet). Two phosphor-coated low-pressure mercury lamps, RPR-3000 (blazed at about 300 nm) and RPR-3500 (blazed at about 350 nm) were used as excitation sources. The products were analyzed on a Hewlett–Packard Model 5890 gas

TABLE 1

Physical Properties of TiO_2 Powder Catalysts

Catalyst[a] (JRC-TIO-)	Surface area (m^2/g)	CO_2 ads. ($\mu mol/g$)	Acid conc. ($\mu mol/g$)	Relative –OH conc.	Band gap (eV)
1 (Anatase)	73	12	—[b]	1.3	3.54
2 (Anatase)	16	1	6	1.0	3.47
3 (Rutile)	51	17	20	1.6	3.32
4 (Anatase)	49	10	5	3.0	3.50
5 (Rutile)	3	0.4	7	3.1	3.09

[a] JRC-TIO-1, -2, and -3 samples were prepared by calcination of the residue from the evaporation of aqueous solution of $Ti(SO_4)_2$. JRC-TIO-4 and -5 samples were prepared by chemical vapor deposition from $TiCl_4$.

[b] Values not measured.

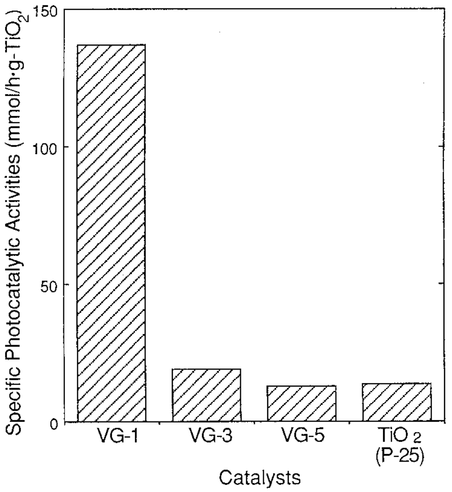

FIG. 2. The specific photocatalytic activity per unit weight of titanium oxide anchored on Vycor glass and as TiO_2 powder (JRC-TIO-4) in the photocatalytic oxidative degradation of 1-octanol under irradiation at around 300 nm.

chromatograph equipped with an Alltech capillary column (0.25 mm × 25 m).

RESULTS AND DISCUSSION

Titanium Oxide Anchored on Vycor Glass

UV irradiation of several Ti/VG catalysts suspended in oxygenated acetonitrile led to the photocatalytic oxidation of 1-octanol to 1-octanal. No products were detected in the dark under these same reaction conditions. Figure 1 shows the time profile for the conversion of 1-octanol under UV irradiation at around 300 nm. Among the three Ti/VG catalysts, Ti/VG-1 exhibited the highest photocatalytic activity, although Ti/VG-1 had the lowest TiO_2 content. The specific photocatalytic activity per unit weight of TiO_2 are shown in Fig. 2 for both the anchored catalysts and a TiO_2 powder (JRC-TIO-4). The titanium oxide clusters bound to the Ti/VG-1 catalyst surface clearly exhibit higher photocatalytic activity (per unit weight) than the TiO_2 powder. These findings indicate that anchoring is a most effective way to prepare an efficient photocatalyst for a liquid-phase reaction. Among Ti/VG catalysts, the photocatalytic activity of the Ti/VG-1 catalyst was much higher than that of Ti/VG-3 or Ti/VG-5. Increasing the number of Ti–O layers of the Ti/VG catalysts caused the photocatalytic activity of the titanium oxide species (per unit weight) to decrease remarkably, presumably because titanium oxides present in inner layers are much less accessible to adsorbates and hence are catalytically inactive.

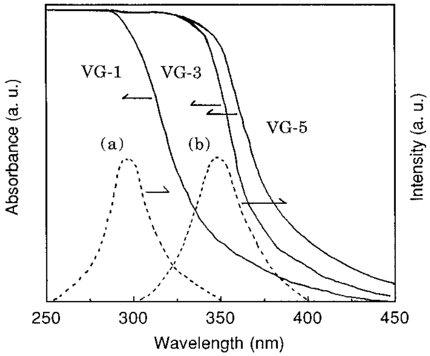

FIG. 3. UV absorption spectra of the titanium oxide anchored onto Vycor glass with a different number of (Ti–O) layers. The wavelength of UV irradiation used is also shown (a and b).

Figure 3 shows the UV absorption spectra of the Ti/VG catalysts with different numbers of (Ti–O) layers. The UV absorption edge of these Ti/VG catalysts is seen at shorter wavelength regions than those of anatase and rutile TiO_2, as would be expected for several clusters. Increasing the number of Ti–O layers of the Ti/VG catalysts caused the UV absorption edge to shift to longer wavelength regions.

Figure 4 shows the XANES and FT-EXAFS spectra of the Ti/VG catalysts and bulk TiO_2 (anatase). Although the bulk TiO_2 exhibits three small preedge peaks in its XANES spectrum, the Ti/VG-1 catalyst exhibits only a single and intense preedge peak similar to that of tetrahedrally coordinated titanium tetra-*i*-propoxide. This observation indicates the presence of tetrahedrally coordinated

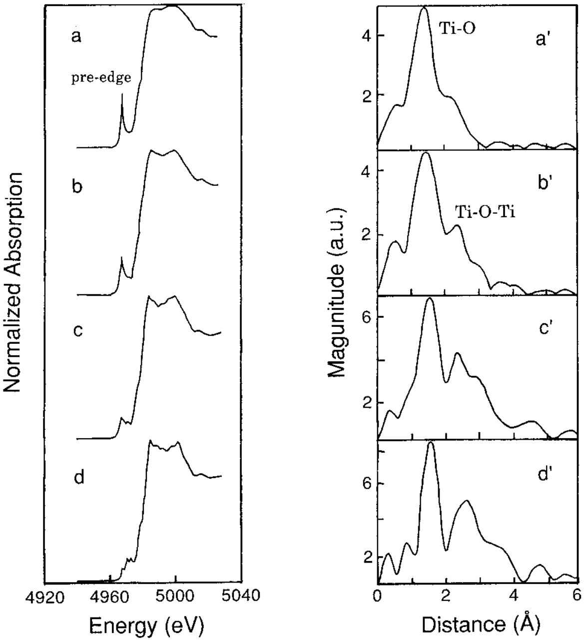

FIG. 4. Ti*K*-edge XANES spectra (left) and FT-EXAFS spectra (right) of the Ti/VG-1 (a, a′), Ti/VG-3 (b, b′), and Ti/VG-5 (c, c′) catalysts, and bulk TiO_2 (anatase) (d, d′).

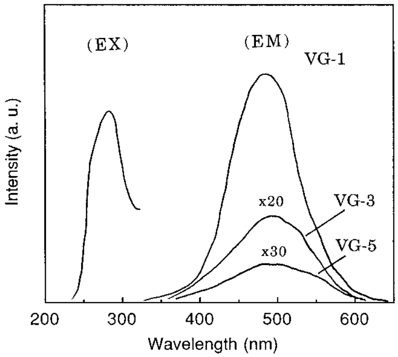

FIG. 5. Photoluminescence and excitation spectra at 77 K of titanium oxide anchored onto Vycor glass with different numbers of (Ti–O) layers.

titanium oxide species on the surface of the Ti/VG-1 catalyst. The FT-EXAFS spectra of the Ti/VG-1 (Fig. 4a′) exhibits only Ti–O peaks, indicating the presence of an isolated titanium oxide species. With Ti/VG-3 and Ti/VG-5 catalysts, the preedge peak becomes weaker in the XANES spectra and other peaks attributed to neighboring titanium atoms (Ti–O–Ti) appeared in the FT-EXAFS spectra. These results indicate that highly dispersed, isolated, tetrahedral titanium oxide clusters were anchored on the Vycor glass and that an increase in the number of Ti–O layers led to aggregation of the isolated titanium species.

Figure 5 shows the photoluminescence spectra of the Ti/VG catalysts, together with their excitation spectra at 77 K. As reported in previous papers (17–19), the absorption of light brings about an electron transfer from the lattice oxygen to the surface-accessible titanium ion, resulting in the formation of a trapped hole (O_L^-) and a trapped electron (Ti^{3+}). The photoluminescence lifetime of the Ti/VG-1 catalyst was 0.54 ms, which was much longer than that of the TiO_2 powder (on the order of nanoseconds). According to our previous observations (8, 18, 19), such long-lifetime photoluminescence is associated with the presence of well-dispersed homogeneous titanium clusters and/or their coordinatively unsaturated ions, rather than with impregnated and/or bulk powder titanium oxides. On the other hand, the photoluminescence intensities of the Ti/VG-3 and Ti/VG-5 catalysts were very weak. Such behavior indicates that highly dispersed isolated titanium oxide species exist only on Ti/VG-1, whereas they exist as aggregates on Ti/VG-3 and Ti/VG-5. This conclusion is in agreement with results obtained from the adsorption spectra of these catalysts. The isolated titanium oxide species on Ti/VG-1 are responsible for its high photocatalytic activity both in the present liquid-phase degradation of 1-octanol and in previously described gas-phase reactions (18, 19).

Standard TiO_2 Powdered Catalysts

UV irradiation of several TiO_2 catalysts in the presence of O_2 led to the oxidation of 1-octanol to produce 1-octanal as the main product, but with relative reactivity and selectivity depending on the specificity of catalysts. The photocatalytic activity induced by UV irradiation at around 350 nm was strongly dependent on the type of TiO_2 catalyst: the observed photocatalytic reactivities were in the order JRC-TIO-4 > -3 > -1 > -5 > -2. The quantum yield determined with the JRC-TIO-4 catalyst in this reaction system under the UV irradiation of light flux of $3 \times 10^{16}\ s^{-1} \cdot cm^{-3}$ was 10%. Those TiO_2 catalysts were also investigated for their relative photocatalytic activity in several gas-phase reactions, i.e., the hydrogenolysis of methyl acetylene with H_2O, the isomerization of 2-butene, and the reduction of CO_2 with H_2O (11). A different order of relative photocatalytic activity was observed for these gas-phase photoreactions: JRC-TIO-4 > -5 > -2 > -3.

We have recently reported that anatase TiO_2 (JRC-TIO-4) with a large band gap and numerous OH groups is more efficient for gas-phase photocatalysis (11). However, in the liquid-phase photocatalytic oxidation of 1-octanol at around 350 nm, the catalyst with a large surface area shows higher photocatalytic activity, irrespective of the band gap or the presence of multiple OH groups. High efficiencies for large surface area catalysts have also been reported in the liquid-phase photocatalytic degradation of 3-chlorophenol on TiO_2 catalyss (20). This suggests that on the interfaces of the catalysts the adsorption and desorption of the reactant molecules from the solution play a significant role in controlling the overall photocatalytic efficiency in liquid samples (21).

The liquid-phase photodegradation of 1-octanol was also carried out under UV irradiation at around 300 nm. At that wavelength the catalytic activity followed the order

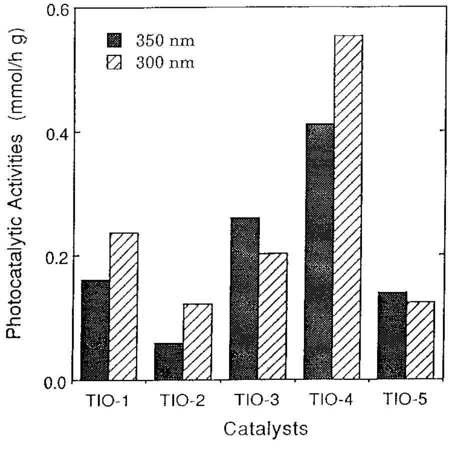

FIG. 6. Photocatalytic degradation of 1-octanol on TiO_2 powder under irradiation at around 350 nm and around 300 nm.

JRC-TIO-4 > -1 > -3 > -5 > -2, which was somewhat different from that observed for reactions induced by UV irradiation at around 350 nm. Figure 6 shows the differences in the product yields observed at these two wavelengths. Those catalysts with the larger band gaps (TIO-2 and TIO-4) exhibited higher activity under UV irradiation at around 300 nm than at around 350 nm.

In conclusion, a large catalyst surface area is a more important factor for achieving high photocatalytic activity by titanium oxide in liquid-phase than in gas-phase photocatalytic reactions. For catalysts with large band gaps, shorter wavelength UV irradiation produces higher photocatalytic activity in both the liquid- and gas-phase reactions.

Anchoring is an attractive method for preparing highly active and stable titanium oxide catalysts. The charge transfer complex formed between surface titanium and oxygen ions, $(Ti^{3+}–O^{-})^*$, plays a significant role as a key active species in liquid-phase photocatalytic oxidations. The titanium oxide species strongly and chemically attached onto the transparent porous Vycor glass resist dissolution in the liquid phase. Therefore, with anchored titanium oxide catalysts, it is unnecessary to filter or separate the catalysts from the liquid phase. This is an important practical advantage for the use of such photocatalysts in the liquid-phase photocatalytic reaction systems.

ACKNOWLEDGMENTS

This work has been supported in part by the Ministry of Education of Japan for Grant-in-Aid Scientific Research (Grants 06239110, 07044162, and 07242264). The work on photocatalysis at the University of Texas is supported by the U. S. Army Research Office. We thank the Japan/U. S. Cooperative Program in Photoconversion and Photosynthesis Research for a fellowship to H.Y. that made his visit to Austin possible.

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