



Photoionization of TiO₂ Particles Incorporated into Silica Gels Studied by EPR Spectroscopy

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Abstract: Titanium dioxide particles with three different average sizes, prepared by three different methods, were incorporated into silica gel pores by impregnation. The titanium dioxide incorporated into the silica gel pores was photoionized by 240-400 nm irradiation at 77 K by a one-photon process to form trapped hole centers on OH group and trapped electron centers on titanium which were detected by electron paramagnetic resonance at 77 K. During the impregnation the smallest size range of TiO₂ particles can be incorporated into silica gels with 2.5-15 nm pores. However, the largest size range of TiO₂ particles can only be incorporated into silica gels with 6-15 nm pores and not into silica gels with 2.5-4 nm pores. The photoyield and stability of photoinduced hole and electron centers depends on the silica pore sizes of silica gels and surface area as well as on the TiO₂ loading. In large pore silica gels and large particle size of TiO₂, photoinduced charge separation reaches to a plateau at shorter irradiation times and the trapped hole and electron centers are more stable to decay.

INTRODUCTION

Photocatalysis of titanium dioxide particles has attracted a great deal of attention in recent years, because TiO₂ has proven to be a promising material as catalysts for solar-assisted decomposition of a variety of undesirable organic compounds in contaminated water and air.^{1,2} The practical application requires the TiO₂ particles of high surface area to be fixed and supported on microporous and mesoporous molecular sieves to increase the access of organic substrates to the catalyst surface to improve the overall efficiency of photocatalytic oxidation.³ Most of the TiO₂-loaded porous materials show higher photo-activity, even at low Ti loading, compared to unsupported TiO₂ alone. The higher photo-catalytic activity of TiO₂

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species supported on porous materials arises from the coordinative unsaturation of Ti ions owing to their high dispersion.⁴

Although previous EPR studies have established the photoactivity of TiO₂ in aqueous solutions,⁵⁻⁸ there have been few studies in solid systems.⁹ Silica gels of average pore diameters from 2.5 to 15 nm should incorporate TiO₂ particles with controlled sizes in the 2.5-15 nm range. In the present work, TiO₂ particles of different pore sizes are prepared by three different methods and incorporated into silica gels of different pore sizes. Photoinduced hole and electron centers trapped in TiO₂ particles are monitored by electron para-magnetic resonance (EPR). The relative photoyield and their stability after irradiation for different TiO₂ loading and for different pore size are investigated.

EXPERIMENTAL SECTION

Synthesis

TiO₂ particles prepared by three different methods were incorporated into the silica gels of 2.5, 4.0, 6.0, and 15 nm average pore diameters by impregnation method. A titania sol (called AT) was prepared by 29.42 mL of Ti[OCH(CH₃)₂]₄ dissolved in 10 mL of absolute ethanol combined with 1 mL of nitric acid dispersed in 200 mL of distilled water with vigorous stirring. The resulting colloidal suspension was refluxed for 8 h at 90 °C. Smaller particle quantum-sized TiO₂ colloids (called QT) were prepared by the following procedure. Distilled water was adjusted to pH 1.5 with nitric acid. A solution of 7.5 mL of Ti[OCH(CH₃)₂]₄ dissolved in 150 mL of absolute ethanol was added dropwise to the acidified water with vigorous stirring. The resulting colloidal suspension was maintained for 10 h with vigorous stirring. To incorporate AT and QT sols, the silica gels was added to the sols (corresponding to TiO₂/SiO₂ = 10 wt %). The final AT/SiO₂ mixture was stirred for 15 h at room temperature and the QT/SiO₂ mixture at 4 °C. The solvent was removed from the final suspension by rotary evaporation at 20 °C for 2-3 h.

The third titania sol (denoted MT) forming the largest TiO₂ particles was prepared and was incorporated into silica gels by the following one-step procedure. 4 g of each silica gel was mixed with a 50 ml aqueous solution containing 1.48 g of (NH₄)₂TiO(C₂O₄)₂·H₂O. The mixture (corresponding to TiO₂/SiO₂ = 10 wt %) was stirred at room temperature for 8 h. The solvent was removed from the suspension by rotary evaporation at 70 °C for 5-6 h.

Finally, all AT/SiO₂, QT/SiO₂, and MT/SiO₂ samples were calcined at 450 °C overnight under flowing oxygen to remove organic materials. The AT-, QT-, and MT-loaded silica gels are designated as AT/SP_x, QT/SP_x, and MT/SP_x samples, respectively, where *x* is average pore diameter in nm.

Sample Treatment and EPR Measurement

For EPR measurement, the silica gel samples incorporated by TiO₂ particles were loaded into 2-mm-i.d. × 3-mm-o.d. Suprasil quartz tubes to about 40 mm in height, could be connected to a vacuum and gas-handling line. Dehydration of the silica gels was carried out by evacuation to 10⁻⁴ Torr at room temperature, followed by gradual heating to 300 °C over a 10 h period. Following this dehydration procedure, the silica gels were treated with 10 Torr of high-purity oxygen at 450 °C overnight to oxidize any titanium species that had been reduced during heating procedure. The oxygen was pumped off at 450 °C, followed by cooling of the sample to room temperature over 4 h under a 10⁻⁴ Torr vacuum. Finally, the sample was sealed in the tube under the vacuum.

A Cermic 150-W xenon lamp (ILC-LX150F) was used for irradiation. The light was passed through a 10 cm water filter and a Corning 7-54 glass filter to give 380 nm irradiation of 1.1×10^6 ergs cm⁻² s⁻¹ in the range from 240 nm to 400 nm. This was sufficient intensity to carry out monophotonic photoionization of TiO₂ particles. Monophotonic photoionization for our system was varified by observing that the photoyield varied linearly with light intensity.

EPR spectrometer was used to detect photoinduced hole and electron centers in TiO₂ particle incorporated into silica gels. EPR spectra were recorded on a Bruker 300 X-band spectrometer with 100 kHz magnetic field modulation. Microwave frequencies were measured with a Hewlett Packard HP 5342A frequency counter, and the magnetic field was calibrated with a Varian E-500 gaussmeter.

RESULTS

The pure silica gels treated by the same procedure as TiO₂ loaded silica gels showed no EPR signal at 77 K or room temperature before and after irradiation at 77 K. The silica gels with TiO₂ particles incorporated by impregnation showed very weak hole signals before irradiation. After being irradiated by 380 nm light at 77 K for 1 s, the TiO₂ loaded silica gels started to show strong EPR signals. The weak hole signals arising before irradiation have the same line shape as those observed after irradiation. The background signals observed before irradiation were subtracted from the observed signals after irradiation to estimate net yield.

AT-Loaded Silica Gels (AT/SPx)

Fig. 1 shows EPR signals observed from silica gels of different pore sizes containing impregnated AT particles after being irradiation by 380 nm light at 77 K for 30 min. The total spectrum is assigned to one hole center on oxygen and two Ti^{III} centers, based on previous works.⁵⁻⁸ The anisotropic line at $g = 2.014$ with a peak-to-peak linewidth of *ca.* 21 G is assigned to oxygen hole centers trapped at the TiO₂ particle surface with an anisotropic g -tensor of $g_z = 2.007$, $g_y = 2.014$, and $g_x = 2.025$.⁶⁻⁸ The rest of the spectra are assigned to two

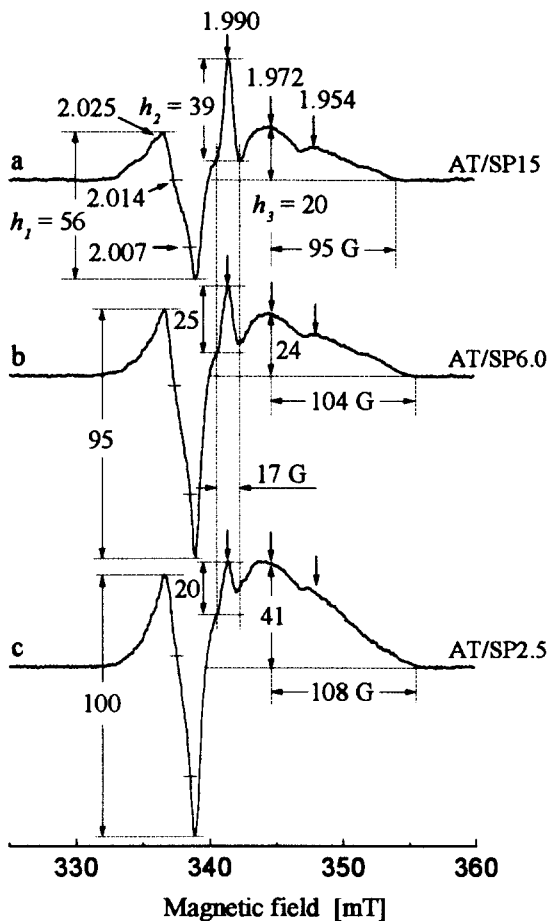


Fig. 1. EPR spectra of samples, (a) AT/SP15, (b) AT/SP6.0, and (c) AT/SP2.5, measured at 77 K immediately after a 380 nm irradiation at 77 K for 30 min.

Ti^{III} centers, one characterized by the sharp peak at $g = 1.990$ from Ti^{III} in the bulk lattice and the other with $g_1 = 1.972$ and $g_2 = 1.954$ from Ti^{III} at the TiO_2 particle surface.⁵⁻⁸ It is apparent in Fig. 1 that the signal intensities of the trapped hole and Ti^{III} centers vary with pore size of the silica gels.

Since the signals arising from the trapped hole and Ti^{III} centers strongly overlap, a reliable, quantitative analysis of their separate signal intensities does not seem feasible. One

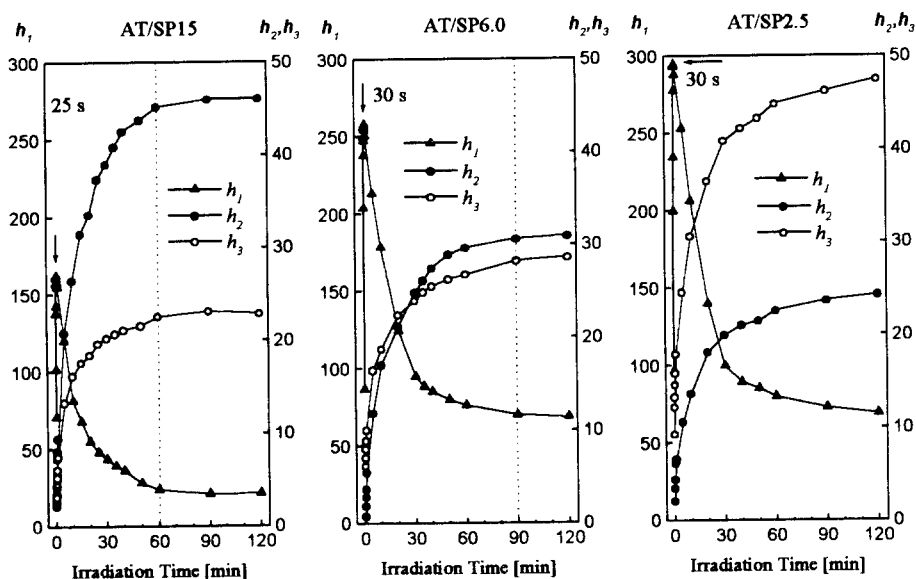


Fig. 2. Variation in relative heights, h_1 , h_2 , and h_3 of hole and Ti^{III} signals measured at 77 K of AT/SP x samples vs. 380 nm irradiation time.

estimate of relative signal intensities of each signal is to compare the heights, h_1 , h_2 , and h_3 defined in Fig. 1, where h_1 measures the hole signal, h_2 measures Ti^{III} in the bulk and h_3 measures Ti^{III} at the surface. These definitions allow an estimate of the intensity changes of each type of signal but do not allow intercomparisons of intensity between signal types because of the spectral overlap.

The variations in h_1 , h_2 , and h_3 in TiO_2 loaded AT/SP15, AT/SP6.0, and AT/SP2.5 samples vs. irradiation time are shown in Fig. 2. After irradiation for just 1 s, the samples start to show strong EPR signals from trapping holes, while a longer irradiation time is needed to observe the EPR signals of Ti^{III} centers. During first 25 s for AT/SP15 and 30 s for AT/SP6.0, and AT/SP2.5, h_1 increases rapidly, reaches a maximum, decreases rapidly and then reaches to a plateau during the next 60 min for AT/SP15 and 90 min for AT/SP6.0, while h_1 for AT/SP2.5 still increases, even after 120 min irradiation. On the other hand, h_2 and h_3 of Ti^{III} increase continuously with irradiation time and reach a plateau after ca. 60 min irradiation for AT/SP15 and ca. 90 min for AT/SP6.0. For AT/SP2.5, h_2 still increases even after 120 min irradiation. For each pore size, the irradiation time required to reach a plateau for h_1 is the same as for h_2 and h_3 . However, the plateau is achieved faster in large-pore silica

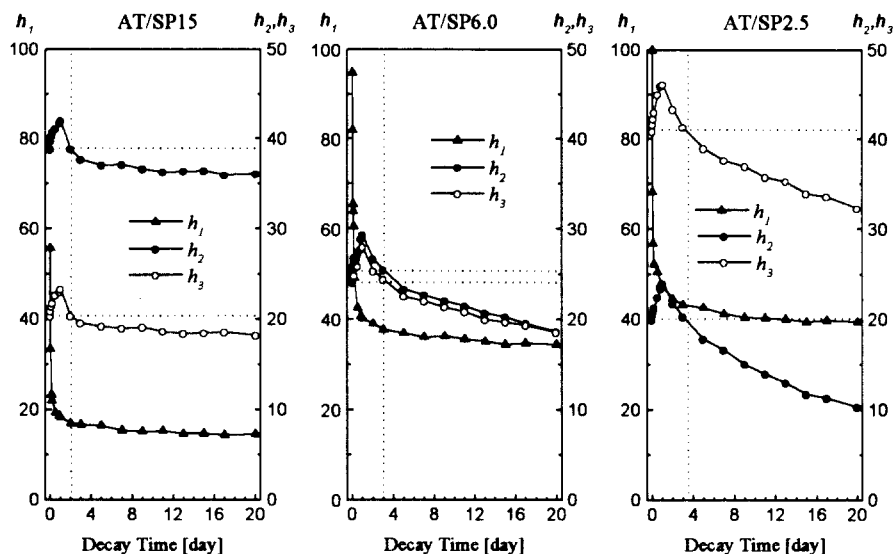


Fig. 3. Variation in relative heights, h_1 , h_2 , and h_3 of hole and Ti^{III} signals measured at 77 K of AT/SP x samples with decay time after 380 nm irradiation at 77 K.

gels. Throughout irradiation time, the intensity of Ti^{III} trapped in bulk lattice is much stronger in large-pore silica gel, whereas the intensities of the hole and Ti^{III} trapped on the surface are much stronger in small-pore silica gel.

The variations in h_1 , h_2 , and h_3 vs. the decay time after irradiation for AT/SP15, of AT/SP6.0, and of AT/SP25 are shown in Fig. 3. For all AT/SP x samples, h_1 decreases rapidly and nearly reaches to a plateau after *ca.* two or three days, while h_2 and h_3 increase slightly for about a day, and then decrease. For the next day in AT/SP15 and for the next two days in AT/SP6.0 and AT/SP2.5, heights h_2 and h_3 decrease to the same heights as measured after 30 min irradiation. The signal intensities of surface and bulk Ti^{III} decrease more rapidly in small-pore silica gel. These results show that impregnation incorporates AT particles into the pore of 15, 6.0, and 2.5 nm silica gels.

QT-Loaded Silica Gels (QT/SP x)

After being irradiated by 380 nm light at 77 K for 30 min, the similar spectra from the QT/SP x samples to those from AT/SP x are observed, as shown in Fig. 4. The g values and lineshapes of the hole center and bulk Ti^{III} in the QT/SP x samples are the same as those of the AT/SP x samples, but the parameters of the surface Ti^{III} in QT/SP x are slightly different from

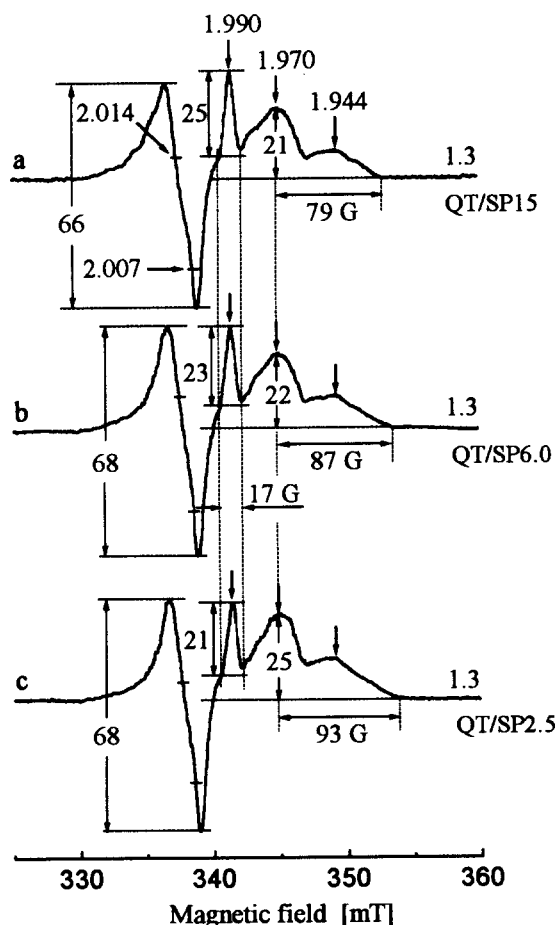


Fig. 4. EPR spectra of samples (a) QT/SP15, (b) QT/SP6.0, and (c) QT/SP2.5 measured at 77 K immediately after a 380 nm irradiation at 77 K for 30 min.

those in AT/SP x . A linewidth measure of the surface Ti^{III} is *ca.* 79, 87, and 93 G in the QT/SP15, QT/SP6.0, and QT/SP2.5 samples, as shown in Fig. 4. These values are all less than those for AT/SP x samples. The intensities of the photoinduced hole and Ti^{III} centers show no big differences between the QT/SP x silica gels of different pore sizes. The height h_1 is similar in all QT/SP x silica gels, while h_2 is slightly higher in large-pore QT/SP x silica gel and h_3 is slightly higher in small-pore QT/SP x silica gels.

The relative heights of the photoinduced EPR signals from trapped hole and Ti^{III} center in QT/SP15, QT/SP6.0, and QT/SP2.5 vs. irradiation time are shown in Fig. 5. The variations in h_1 , h_2 , and h_3 are similar to those in the AT/SPx samples, but irradiation times for reaching maxima and plateaus are different. After irradiation for 30 s in QT/SP15 and 40 s in QT/SP6.0 and QT/SP2.5, h_1 reaches a maximum. After irradiation for *ca.* 90 min in QT/SP15, h_1 , h_2 , and h_3 reach plateaus, while for QT/SP6.0 and QT/SP2.5 the signal continues to decrease even after 120 min. The intensity of the bulk Ti^{III} center is slightly stronger in large-pore silica gel, whereas the intensities of the hole and the surface Ti^{III} center are slightly stronger in small-pore silica gel.

The relative heights of EPR signals measured at 77 K vs. decay time after irradiation at 77 K are shown in Fig. 6 for QT/SP15, QT/SP6.0, and QT/SP2.5. The height h_1 decreases rapidly and then reaches a plateau after *ca.* three to six days, while h_2 and h_3 increase somewhat for a day. For the next day, in QT/SP15 and in QT/SP6.0, and for two days in QT/SP2.5, h_2 and h_3 decrease to the same heights as after 30 min irradiation. The signal intensities of the surface and bulk Ti^{III} centers decrease more rapidly in small-pore silica gel. These results show that impregnation incorporates QT particles into the pore of 15, 6.0, and 2.5 nm silica gels.

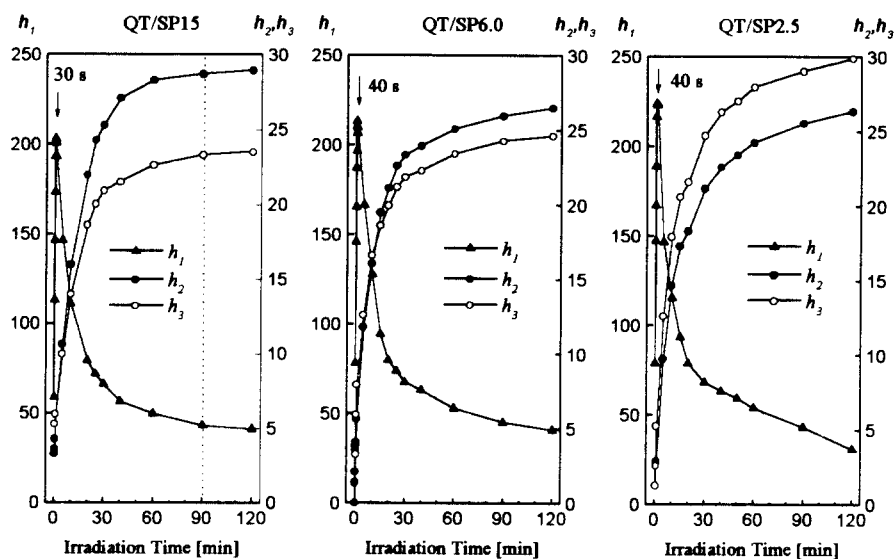


Fig. 5. Variation in relative heights, h_1 , h_2 , and h_3 of hole and Ti^{III} signals measured at 77 K of QT/SPx samples vs. 380 nm irradiation time

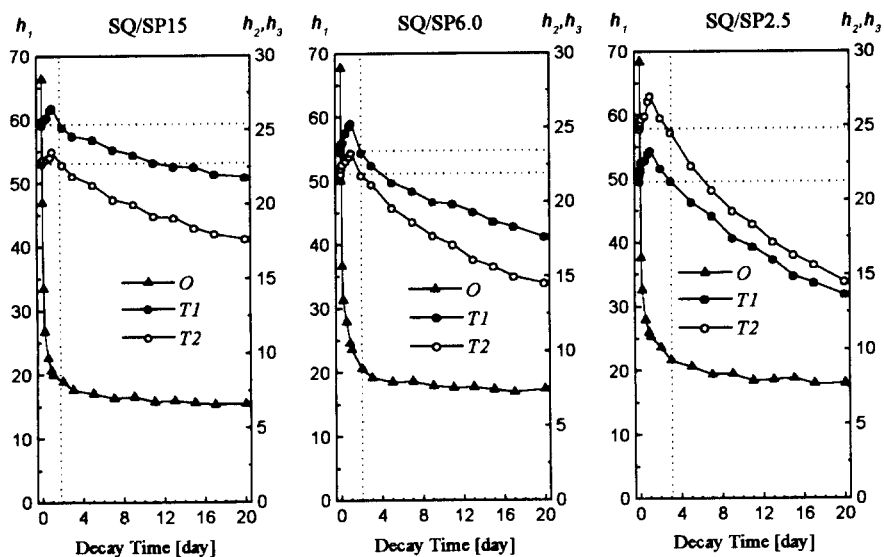


Fig. 6. Variation in relative heights, h_1 , h_2 , and h_3 of hole and Ti^{III} signals measured at 77 K of QT/SPx samples with decay time after 380 nm irradiation at 77 K.

MT-Loaded Silica Gels (MT/SPx)

Fig. 7 shows EPR spectra observed from the MT/SPx samples after being irradiated by 380 nm light at 77 K for 30 min. The linewidth of the surface Ti^{III} center is 86 G, which is similar to that of the QT system but less than that in AT system. Although the intensity of the surface Ti^{III} center is similar in both MT/SP15 and MT/SP6.0 samples, the intensities of the hole center and the bulk Ti^{III} center in MT/SP15 are stronger than those in MT/SP6.0. It is noticeable that only very weak EPR signals are observed from MT/SP4.0. A similar weak spectrum was also obtained from MT/SP2.5. This indicates that the 2.5 and 4.0 nm pore diameters of the silica gels are not large enough to accommodate MT particles in the pores by impregnation, and that the MT particles are also not adsorbed significantly on the external surface.

The variations of relative heights of the EPR signals in MT/SP15 and MT/SP6.0 vs. irradiation times are shown in Fig. 8. After first 20 s for MT/SP15 and 30 s for MT/SP6.0, the height h_1 reaches a maximum. All the heights, h_1 , h_2 , and h_3 , reach a plateau after ca. 30 min for MT/SP15 and 50 min for MT/SP6.0. During irradiation, the intensities of the hole and the bulk Ti^{III} center are much stronger in large-pore silica gel, whereas the intensity of the

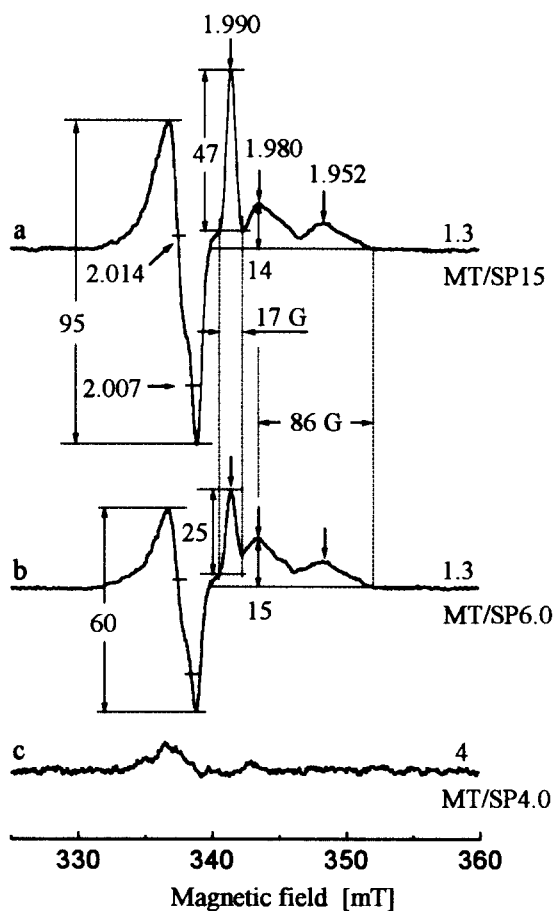


Fig. 7. EPR spectra of samples (a) MT/SP15, (b) MT/SP6.0, and (c) MT/SP2.5 measured at 77 K immediately after a 380 nm irradiation at 77 K for 30 min.

surface Ti^{III} center is similar in both MT/SP15 and MT/SP6.0.

The variations of relative heights, h_1 , h_2 , and h_3 for EPR signals measured at 77 K vs. decay time after 380 nm irradiation are shown in Fig. 9 for MT/SP15 and for MT/SP6.0. The height h_1 decreases rapidly for *ca.* two or three days, whereas h_2 and h_3 increase for *ca.* 12 h, and then decrease slightly. The initial increases in h_2 and h_3 are higher in large-pore

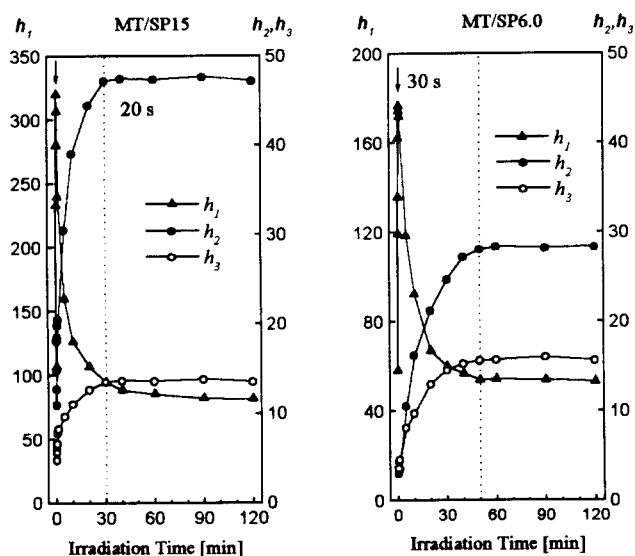


Fig. 8. Variation in relative heights, h_1 , h_2 , and h_3 of hole and Ti^{III} signals measured at 77 K of MT/SPx samples vs. 380 nm irradiation time.

silica gels, unlike in AT/SPx and QT/SPx. For the next 12 h, h_2 and h_3 decrease to the same heights as after 30 irradiation. Photoinduced hole and Ti^{III} centers in MT/SP15 are more stable than those in MT/SP6.0. These results show that impregnation incorporates MT particles into the pore of 15 nm and 6.0 nm silica gels, but not into 4.0 nm and 2.5 nm silica gels.

DISCUSSION

Irradiation of TiO_2 particles incorporated into silica gels with light of 380 nm or shorter wavelength generates electron-hole pairs which diffuse apart. The pairs are trapped as hole centers on oxygen and electron centers on Ti^{IV} to give Ti^{III} . The paramagnetic centers are observable by EPR and have been assigned to holes trapped on surface OH group as a $(\text{TiO}_2)_{\text{latt}}\text{Ti}^{\text{IV}}\text{O}\cdot$ radical,⁶⁻⁸ and to electrons trapped on Ti^{IV} ions in the bulk lattice $[(\text{Ti}^{\text{III}})_{\text{latt}}]$ and at the surface $[(\text{Ti}^{\text{III}})_{\text{surf}}]$.⁵⁻⁸

Additional evidence for the assignment of the Ti^{III} peaks at $g = 1.972$ and 1.954 to a surface Ti^{III} species is shown in Table 1. Table 1 shows a linewidth parameter for surface Ti^{III} which is defined in Fig. 1 and pH of $\text{TiO}_2/\text{silica}$ gels (5 g of $\text{TiO}_2/\text{silica}$ gels l^{-1})

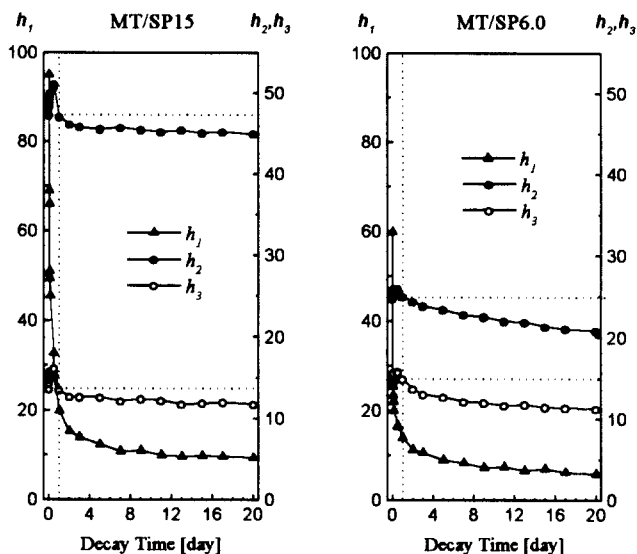


Fig. 9. Variation in relative heights, h_1 , h_2 , and h_3 of hole and Ti^{III} signals measured at 77 K of MT/SP x samples with decay time after 380 nm irradiation at 77 K.

suspended in distilled water. Before calcination, the pH values are independent of pore size. After calcination, the pH values increase with pore size for AT and QT TiO₂ particles. These pH changes anticorrelate with the lineshape parameter for surface Ti^{III}. This indicates that the surface environment of AT and QT TiO₂ particles changes during calcination, depending on pore size, which supports the assignment of the spectrum at $g = 1.972$ and 1.954 to surface Ti^{III} centers. In contrast, the lineshape of the $g = 1.990$ center does not change significantly with pore size or pH change, which supports its assignment to bulk Ti^{III} centers. Possible bulk and surface sites for trapped holes are not distinguished in the EPR spectrum. In the TiO₂-loaded silica gels, there exist two kinds of hydroxyl groups, one at the silica gel surface and the other at TiO₂ surface. The hydroxyl groups at the TiO₂ surface act as hole-trapping site, as discussed previously.⁶⁻⁸ In other work, the hydroxyl groups at the silica gel surface have been found to act as electron accepters¹² to form hydrogen atoms, which are stably trapped at 77 K in the silica gel surface and detected by EPR. The hydrogen atom signal intensity depends remarkably on the pore size.¹² Such trapped hydrogen atom spectra are not observed in the TiO₂-loaded silica gels in this study. This seems to indicate that the Ti^{IV} ions in the TiO₂ particles are better electron acceptors than the hydroxyl groups at the silica gels surface.

Table 1. EPR linewidth of Ti^{III} signal arising from the electrons trapped at the surface of TiO_2 at different pH.

samples	pH ^a		ESR line width [G]
	Uncalcined	Calcined	
AT/SP15	2.9	4.2	95
AT/SP6.0	2.9	3.5	104
AT/SP2.5	2.8	3.2	108
QT/SP15	2.6	5.4	79
QT/SP6.0	2.6	3.6	87
QT/SP2.5	2.5	3.0	93
MT/SP15	3.5	3.7	86
MT/SP6.0	3.4	3.5	86
MT/SP2.5	3.3	3.4	—

^aMeasured from suspensions dissolved TiO_2 -loaded silica gels in distilled water with 0.5 g of TiO_2/L . Their maximum uncertainties are ± 0.1 .

The observed pore-size effect provides evidences that the silica gels incorporate AT, QT, and MT TiO_2 particles within their pores except that MT particles are too large to be incorporated into 4.0 and 2.5 nm pores. During impregnation, all QT particles ranging from 2 nm to 4 nm in diameter¹¹ are incorporated into the 2.5-15 nm silica gel pores. The average AT particle sizes are larger than the QT particles, based on a cloudy AT sol compared to a transparent QT sol. Since strong EPR signals are observed from AT loaded silica gels of 2.5-15 nm pore sizes, It appears that the smallest AT particle size is less than 2.5 nm. As shown in Fig. 7, no EPR signal was observed from MT-loaded silica gels with 4.0 and 2.5 nm pores, but strong EPR signals are observed from 6.0 and 15 nm pores. This indicates that the smallest MT particle diameters are larger than 4.0 nm and smaller than 6.0 nm.

The signal intensities of the hole and Ti^{III} centers in the TiO_2 -loaded silica gels of different pore sizes are mainly affected by the pore size and by TiO_2 particle size. In the large-pore silica gel, the origin of the stronger intensity of the bulk Ti^{III} center is unclear. The signal intensities from AT- and MT- loaded silica gels are more strongly affected by pore size than those of QT-loaded silica gels. This indicates that the AT and MT particles are larger than the QT particles. This result is consistent with our conclusions above.

As shown in Fig. 2, 5, and 8; after reaching a maximum for the first 20 to 40 s of irradiation, the intensity of the hole center decreases rapidly, while the intensities of the surface and bulk Ti^{III} centers increase continuously, until the intensity of the hole center

reaches a plateau. During the first 20 to 40 s, the photogenerated electrons are not observable by EPR. During the next 60 min of irradiation, some electrons seem to recombine with the hole center to cause a large decrease while electrons are trapped by bulk and surface of Ti^{IV} to form Ti^{III} and achieve net charge separation.

As shown in Fig. 3, 6, and 9; the intensity of hole centers decreases to a plateau after standing in dark for two to six days for AT/SPx, MT/SPx, and QT/SPx samples, while intensities of the bulk and surface Ti^{III} centers increase slightly after 12 h in MT/SPx and after 24 h in AT/SPx and QT/SPx samples before decay occurs. The increase is higher in small-pore silica gel for AT/SPx and QT/SPx but in large-pore silica gel for MT/SPx samples which show stronger hole signal. Mobil electrons may contribute to an increase in the Ti^{III} signals and may recombine with hole trapping sites.

In summary, during the impregnation of the silica gels of 2.5-15 nm pore size, QT and AT TiO₂ particles are incorporated into all pores, while MT TiO₂ particles are too large to be incorporated into 4 nm and smaller pores. The photoinduced hole centers and surface Ti^{III} centers increase in intensity with decreasing pore size for AT/SPx and QT/SPx samples. Photoinduced charge separation reaches a plateau at shorter irradiation time and is more stable to decay for the larger TiO₂ particles.

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