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Effect of Calcination Temperature and Addition of Silica, Zirconia, Alumina on the Photocatalytic Activity of Titania

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Abstract–Nanophase titania was prepared by sol-gel method and spray pyrolysis. We tried to elucidate the relationship between the photoactivity and the crystallite size of anatase phase. To better understand the changes in the bulk and the surface of titania as the calcination temperature is changed, EPR and photoluminescence analysis were carried out. The effect of the secondary metal oxide embedded into titania matrix on the photoactivity was also investigated. It was found that the photoactivity of titania has a linear relationship to the crystallite size. For the analysis of EPR and photoluminescence for pure titania, the increase of photoactivity with increasing the calcination temperature is due to the formation of surface active sites such as O^- as well as the increase of crystallinity resulting from the removal of bulk defects. For silica/titania mixed oxide, it was found that the improvement of the thermal stability of anatase phase is important to enhance the photoactivity of titania because the prepared catalyst was calcined at a higher temperature than 700 °C without forming rutile phase. It was also concluded that the simultaneous increase of the surface area and the crystallinity promises to improve the photoactivity achieved by increasing the content of silica up to 60%. By the analysis of EPR and photoluminescence, it was found that the embedding of silica into titania matrix suppresses the formation of Ti^{3+} and produces a new active site of Ti-O-Si, which easily interacts with the oxygen. In the investigation of zirconia/titania and alumina/titania mixed oxide, it was found that the increase of the surface OH is essential to positively affect of the improved thermal stability on the photoactivity.

Key words: Titania, Sol-Gel Method, Mixed Oxide, EPR, Photoluminescence

INTRODUCTION

Titania is well know to have high photocatalytic activity [Pruden and Ollis, 1983; Hoffman et al., 1995]. When titania is illuminated by suitable light energy (hν) higher than its band gap, electrons in the valence band are excited and jump up to the conduction band resulting in generating positive holes in the valence band. Some portion of the photo-excited electrons and holes are diffused to the surface of titania and take part in the chemical reaction with the adsorbed electron acceptors or donors, respectively. Unfortunately, most of photo-excited electron and hole pairs are consumed by the volume recombination process in the bulk. So, in order to improve the photoactivity, it is essential to increase the portion of electron and hole pairs transferred to the adsorbed redox species as well as to suppress the recombination processes.

For the bulk titania particles, the most photo-excited electron and hole pairs are consumed by the volume recombination at bulk defect sites. Therefore, it is very important to reduce the bulk defect for high photoactivity. The best way to reduce the volume recombination of photo-excited electron and hole pairs is to increase the crystallinity of titania. There are many reports relating to the crystallinity effect on the photoactivity of titania particles [Nishimoto et al., 1985; Ohtani et al., 1997; Rivera et al., 1993; Porter et al., 1999; Zhang et al., 2000]. Higher crystallinity of anatase phase leads to higher photoactivity. When titania is prepared by a liquid technique such as sol-gel synthesis, the post heat treatment temperature is crucial to the photoactivity because it changes the crystallinity as well as the crystal structure of titania. Higher crystallinity needs higher calcination temperature. But, the increase of calcination temperature to improve the crystallinity of titania prepared by a liquid phase technique is limited because anatase phase is thermally unstable and turned into rutile phase which is less photoactive. Thus the major goal of this work is to improve the thermal stability of titania for the phase transition.

The use of mixed oxide or multicomponent oxide as a photocatalyst is a novel class in recent years. The key concept for the modification of titanium oxide with other oxides such as Fe_2O_3, SiO_2, ZrO_2, Al_2O_3, Nb_2O_5, WO_3, and MoO_3 is to change the surface or structural properties and the photochemical property to improve its photoactivity [Navio et al., 1996; Negishi et al., 1994; Inoue et al., 1994; Anderson and Bard, 1997; Yamashita et al., 1998; Fu et al., 1996; Cui et al., 1995; Do et al., 1994; Papp et al., 1994; Lee et al., 1993]. Especially, titania-silica materials have been extensively used as catalysts and supports for a wide variety of reactions [Thangaraj et al., 1991; Cauqui et al., 1992; Klein et al., 1996]. Fig. 1 illustrates the research area of silica-titania materials. The unique physico-chemical properties of titania-silica materials as a photocatalyst are associated with the support effect and the quantum-size effect. The silica/titania mixed oxides as a photocatalyst are classified into three categories in terms of the type of mixed structure as shown in Fig. 1. In the field of photocatalysts, there has been no attempt to use the mixed oxide of type B. There are a few reports about the use of silica/titania mixed oxide with the type A and C as a photocatalyst

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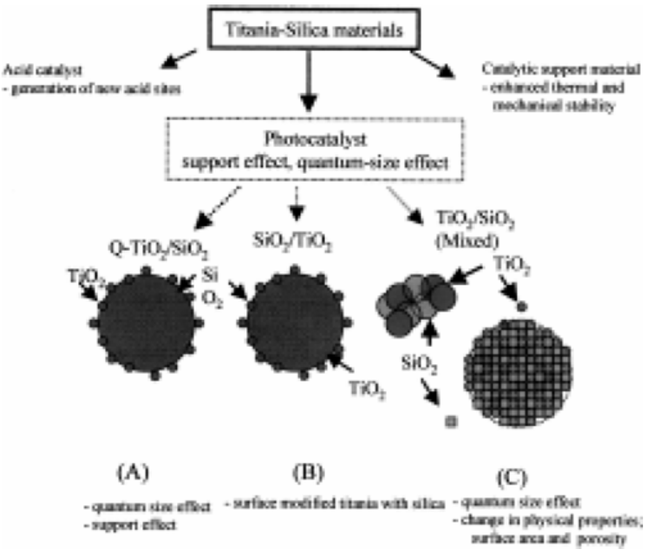


Fig. 1. Schematic diagram showing the research field of silica/titania mixed oxide.

[Anpo et al., 1986; Inoue et al., 1994; Anderson and Bard, 1995; Fu et al., 1996]. The photoactivity of each type of silica/titania mixed oxide is different from each other and strongly affected by how it is made and what the reaction system is.

Viswanath and Ramasamy prepared a titania-silica nanocomposite by a sol-gel method [Viswanath and Ramasamy, 1998]. The composite (titania/silica=80/20) has pure anatase phase even though the calcination temperature was 900 °C. From this report, we try to increase the thermal stability of titania by embedding the secondary metal oxide into titania matrix like the mixed type C in Fig. 1.

In this work, nanophase titania was prepared by the sol-gel method and the effect of the calcination temperature on its photoactivity was monitored. In order to improve the photoactivity, we tried to improve the thermal stability of titania by embedding the secondary metal oxides such as silica, zirconia, and alumina. We also tried to clarify the relationship between the photoactivity and the crystallinity of titania. To achieve this objective, it is necessary to control the crystallinity at a fixed particle size and surface area. So, the spray pyrolysis technique was introduced because the process can easily control the particle size by changing the concentration of precursor solution [Messing et al., 1993; Kang et al., 1999]. To better understand the change in the bulk and the surface of titania prepared by the sol-gel method, EPR analysis and photoluminescence measurement were carried out.

EXPERIMENTAL

1. Preparation of Titania and M_xO_y/TiO_2 (M_xO_y=SiO_2, ZrO_2, and Al_2O_3) Mixed Oxide by Sol-Gel Method

Titanium ethoxide (TEOT, Ti-20% Aldrich), tetraethylorthosilicate (TEOS, 98% Aldrich), zirconium (IV) propoxide (ZTP, 70 wt% Aldrich), and aluminum isopropoxide (AIP, 98% Aldrich) were used as the precursor of titania, silica, zirconia, and alumina, respectively. The hydrolysis of alkoxide precursor was carried out in excess water with acidic catalyst. All preparation conditions are listed in Table 1.

Table 1. Preparation condition of titania baded photocatalyst by the sol-gel method

Catalyst	Precursor	H_2O/M^+	H^+/M^+	Et-OH/M^+
TiO_2	TEOT	100	0.2	1
SiO_2/TiO_2	TEOT&TEOS	150	0.2	1
ZrO_2/TiO_2	TEOT&ZTP	180	0.95	1
Al_2O_3/TiO_2	TEOT/AIP	180	0.5	1

For the preparation of pure titania particle, the precursor was added into the premixed solution of water, HCl, and the corresponding alcohol at the room temperature. This solution was mixed for 24 hours and heated at 80 °C for 5 hours to remove the added and produced alcohol. The alcohol-removed titania sol solution was dried in an oven at 100 °C. The obtained xerogel was calcined at 300 to 600 °C.

In the preparation of X-silica/titania (X means the atomic % of the second metal oxide with respect to titania), X-zirconia/titania, and X-alumina/titania mixed oxides, the overall procedure is same to that of pure titania. The only difference is that the precursor of silica, zirconia, and alumina was hydrolyzed in the first step with the pre-mixed water solution, which contains hydrochloric acid and ethanol. After two precursors were added in the pre-mixed solution, it was maintained for 24 hours at the room temperature. The M_xO_y/TiO_2 xerogel obtained after drying was calcined at 500 to 800 °C. The content of silica with respect to titania was varied from 10 to 60 at.%. For the zirconia/titania mixed oxides, the zirconia content was fixed at 10%. The content of alumina was also varied from 2 to 30 at.%.

2. Preparation of TiO_2 by the Spray Pyrolysis

Titanium ethoxide of 25 ml was dissolved in the purified water 500 ml containing excess nitric acid under vigorous stirring by a magnetic stirrer for 1 hour. Then after, a hydrolyzed clear titanium precursor solution was obtained without any precipitates, the clear solution was atomized by a nebulizer (1.67 MHz) to form droplets. The produced droplets were carried into the hot furnace with the length of 80 cm by the carrier gas (air) which is maintained at 3 l/min. The temperature of furnace was varied from 500 to 900 °C. The produced titania particles were collected with thimble filter (28×100 mm, Toyo Roshi Kaisha Ltd.).

3. Analysis

The major phase of prepared titania based photocatalyst was analyzed by Rigaku D/MAX-III (3 kW) diffractometer using Cu Kα (λ=0.1506) radiation. The crystallite size was calculated from the broadening of the anatase main peak at 2θ=25.3° by using the Schrerrer formula. The percentage of rutile phase was calculated by the following equation [Fu et al., 1996].

$$\%\ \text{of rutile} = \frac{1}{\frac{A}{R}\times 0.884 + 1}\times 100$$

where A and R are the peak area for the major anatase (2θ=25.3°) and rutile phase (2θ=25.5°).

The adsorption-desorption measurement of nitrogen was performed by Micrometrics ASAP 2400. Surface area was calculated by using the BET equation as determined by the adsorption isotherm. The average particle size of titania prepared by the spray pyrolysis was estimated by scanning electron microscopy (SEM, Philip

SEM-535M).

To measure the relative quantity of surface OH groups, FT-IR spectra of all prepared titania based photocatalysts were obtained by Bomen MB-100 spectrometer. The existence of Ti-O-Si bond was also confirmed by FT-IR analysis.

For pure titania and silica/titania mixed oxide, X-band EPR measurements (BRUKER, 9.424 kHz) at 77 K were carried out to investigate the change of paramagnetic species. The g-factors were calibrated by comparison to a powder 1, 1-diphenyl-2-picrylhydrazyl (DPPH) radical sample.

The photoluminescence spectra of titania particles prepared by the sol-gel method were measured at 77 K using a Shimadzu RF-5000 spectrophotofluoremeter. Titania samples were thermally treated before the measurement of photoluminescence. In the first step, all samples, which were loaded in a quartz tube, were evacuated up to 10^{-5} torr at 300 °C to remove the attached OH groups or water vapor. These thermally treated samples were cooled to the room temperature and refilled with the oxygen of 200 torr. The oxygen-filled sample tube was maintained at 200 °C for 2 hours to oxidize the carbon compound remaining on the surface of titania. Finally, all sample tubes were evacuated up to 10^{-5} torr at 200 °C and used for the measurement of photoluminescence. The quenching of photoluminescence was carried out by using the oxygen of 20 torr.

The photocatalytic activity of prepared titania based photocatalyst was measured by the decomposition of trichloroethylene (TCE). A batch-circulating reactor was used. Each prepared photocatalyst (0.5 g/*l*) was dispersed into purified water of 750 ml. The initial concentration of TCE was 37 ppm. The solution was irradiated by ultraviolet light with the wavelength ranging from 300 to 400 nm. The change in the concentration of TCE with the reaction time was monitored by Cl^- electrode (Orion, model 96-17B).

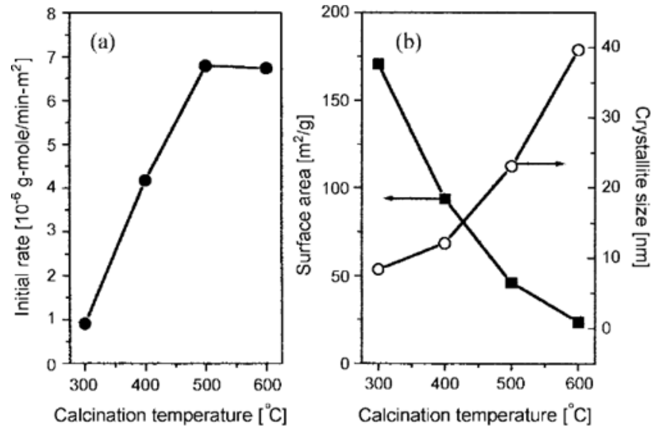


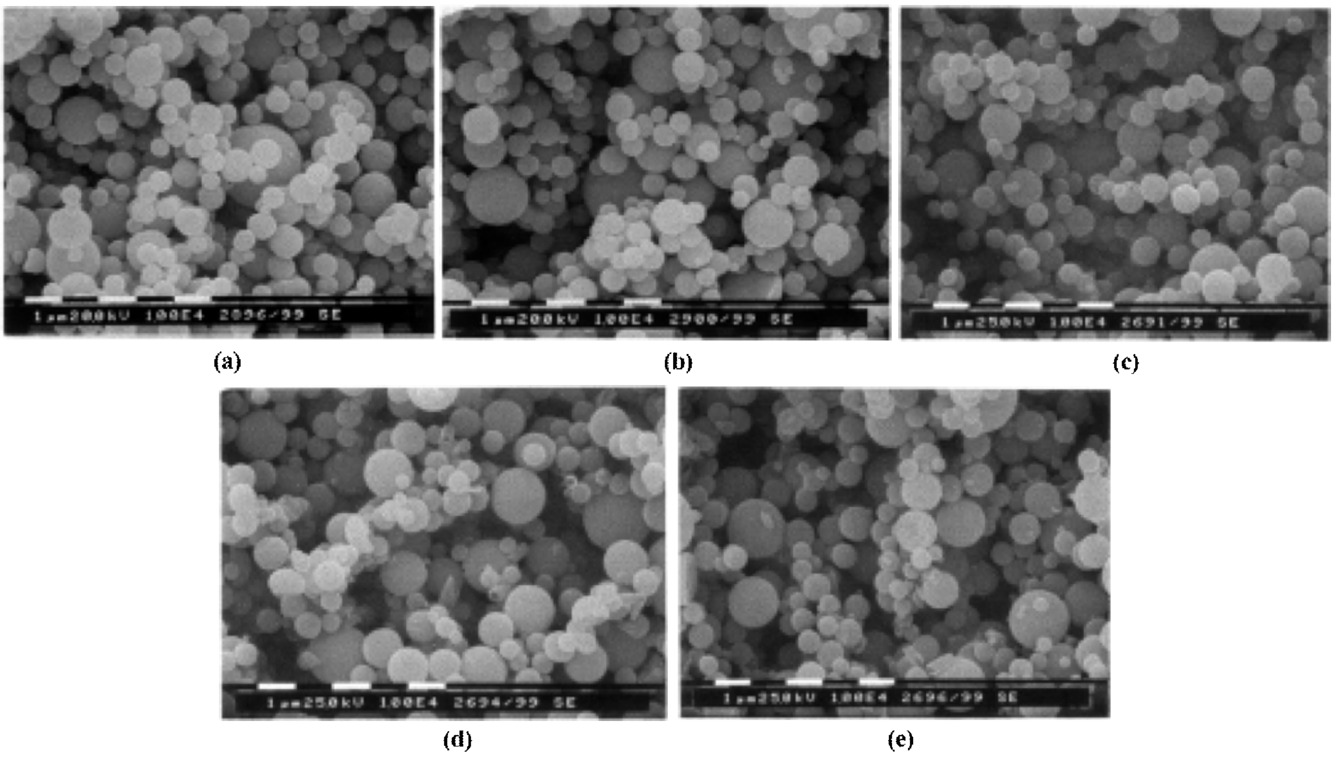
Fig. 2. The photocatalytic activity (a) and the change of surface area and crystallite size of anatase phase (b) as a function of calcination temperature for titania particles prepared by the sol-gel method.

RESULTS AND DISCUSSION

1. Photocatalytic Activity of Titania

1-1. Effect of Calcination Temperature

The photoactivity of as-prepared titania is shown in Fig. 2(a) as a function of calcination temperature. The changes in crystallite size and surface area of titania particles are also presented in Fig. 2(b).


(a) (b) (c)

(d) (e)

Fig. 3. SEM photographs of titania particles prepared by the spray pyrolysis at several temperatures; (a) 500 °C, (b) 600 °C, (c) 700 °C, (d) 800 °C, and (e) 900 °C.

The photoactivity of titania for the decomposition of TCE is increased and saturated as the calcination temperature increases up to 600°C. The crystallite size of anatase phase monotonically increases with increasing the calcination temperature, whereas the surface area is reduced dramatically. According to the XRD analysis for all prepared titania particles, no rutile phase was observed up to 500°C. However, at 600°C, some rutile phase was formed. Therefore, the saturation of the photoactivity with increasing the calcination temperature is due to the formation of rutile phase. Given that the photoactivity is enhanced with increasing the calcination temperature although the surface area is reduced, it is clear that the crystallinity of titania is a more important factor than the surface area. Also, it is necessary to increase the crystallinity by calcining the as-prepared titania at as high a temperature as possible in order to obtain high photoactivity.

1-2. Relationship Between the Crystallite Size of Anatase Phase and the Photoactivity

The increase of crystallite size represents the increase of crystallinity in this work. This argument is acceptable when the increase of crystallinity is achieved by the post heat treatment for titania particles prepared by the sol-gel method. When the crystallinity of titania is controlled by calcination, the changes in the particle size and the surface area are inevitable. So, it is required to control the crystallite size without the change of surface area and particle size in order to precisely investigate the effect of crystallinity. In this work, the spray pyrolysis is introduced to control the crystallinity of titania at a fixed particle size and surface area.

Fig. 3 shows SEM photographs for titania particles prepared by the spray pyrolysis. The prepared titania particles have a spherical shape, and no significant change of the particle size is observed. All physical properties for the as-prepared titania particles are summarized in Table 2. The photocatalytic activity of titania particles prepared by the spray pyrolysis is also listed in Table 2. Up to 800 °C, the formation rutile phase is not significant less than 10%. When the preparation temperature is 900°C, 20% rutile phase is formed. The crystallite size is increased from 10 nm to 35 nm as the preparation temperature increases. With changing the preparation temperature, the change of surface area is not significant. Therefore, the crystallite size of titania was controlled by spray pyrolysis at the fixed particle size (0.6 μ estimated from SEM results) and surface area (2.5±0.1 m^2/g from BET analysis).

The dependency of photoactivity on the crystallite size of anatase phase is shown in Fig. 4(a) for titania particles prepared by spray pyrolysis. The photoactivity (g-moles/min-m^2) linearly increases with increasing the crystallite size. This linear relationship between the photoactivity and the crystallite is also found in the result of sol-gel derived titania as shown in Fig. 4(b). From this result, we conclude that the photoactivity of pure titania could be enhanced by increasing the crystallite size of anatase phase as long as no significant rutile phase is formed.

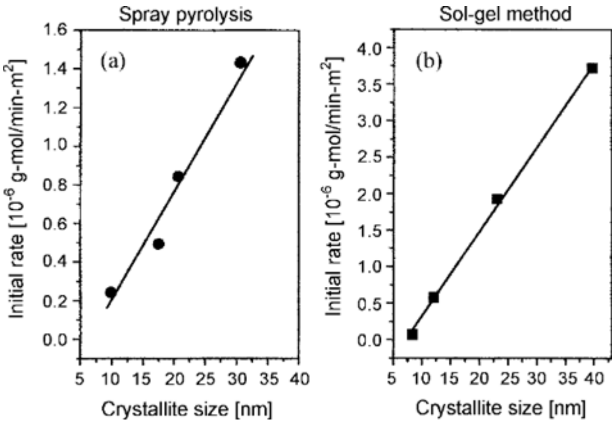


Fig. 4. Relationship between the photoactivity and the crystallite size of titania prepared by the spray pyrolysis (a) and the sol-gel method (b).

1-3. Effect of Calcination Temperature on the Behavior of Ti^{3+} and O^- or O_2^-

For bulk titania, the most consumption of photo-excited electron and hole pairs is achieved by volume recombination at the low coordinated Ti^{3+} sites. Therefore, the suppression of the volume recombination for bulk titania of large particle size is crucial to achieve the high photoactivity. The validity of this argument is identified by the test of photoactivity for titania particles prepared by the sol-gel method in the previous chapter 1.1. Thus, the improvement of the photoactivity of titania prepared by the sol-gel method with increasing the calcination temperature (Fig. 2) results from the enhancement of the crystallinity, which means the reduction of bulk defect sites.

When considering that the photoactivity of titania prepared by the sol-gel method increases with increasing the calcination temperature although the surface area is reduced, it is expected that the reduced surface is turned to be more advantageous for photoactivity. Therefore, in this work, the changes in the bulk and the surface of titania prepared by the sol-gel method are monitored by EPR study in order to better understand the improvement of photoactivity as the calcination temperature increases.

Fig. 5 shows the EPR spectra measured at 77 K for titania samples with different calcination temperatures. In general, the signal at a g-value greater than 2.003 (free electron) is due to anion species such as O^-, whereas a g-value smaller than 2.0023 assigns the cation species such as Ti^{3+}. The greatest change in EPR spectra is observed at g=1.992 assigned to bulk Ti^{3+}. Referring to the literature [Howe and Graetzel, 1987; Nakaoka and Nosaka, 1997], this peak

Table 2. Preparation properties and photocatalytic activity of TiO_2 prepared by the spray pyrolysis

Temperature (°C)	% of Rutile	Crystallite size (nm)	Initial rate (10^{-6} g-mol/min)	Surface area (m^2/g)
500	0	9.9	1.4	2.4
600	1.48	17.5	3.0	2.4
700	7.58	20.7	5.2	2.5
800	10	30.6	9.2	2.6
900	20	35.5	6.0	2.4

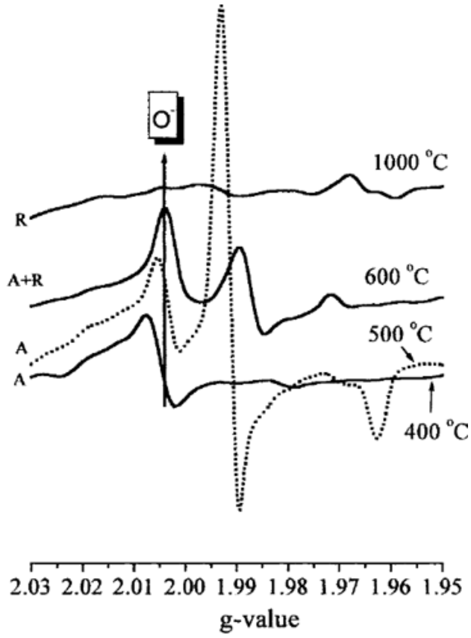


Fig. 5. EPR spectra measured at 77 K under air environment for TiO_2 prepared by the sol-gel method.

(g=1.992) is contributing to the bulk Ti^{3+} defect. The bulk defect is formed and removed finally by elevating the temperature. One should notice that pure rutile phase has no signal assigning the surface O^- around g=2.004.

The bulk defect and the surface defect give different EPR signals. The positions of EPR peak for each defect sites are identified by changing the surface state. The signal position assigned to the surface defects is grown after removing the electron and hole scavengers which are attached on the surface of titania. Fig. 6 shows the EPR spectra of titania particles measured after heat treatment at 300 °C under a vacuum condition. The peak at g=1.969 and the shoulder peak at g=1.986 also increases after heat treatment at 300 °C under a vacuum condition. No significant change in the peaks at g=1.992 and 1.963 is observed. From these changes, we confirmed that the peaks at g=1.986 and 1.969 are due to the surface Ti^{3+} defect and the peaks at g=1.992 and 1.963 are responsible for the bulk Ti^{3+} defect. From the EPR study, it is clear that trapping sites of photo-excited electron/hole pairs are simultaneously formed on the surface and in the bulk of titania particles during the calcination process. But, the bulk defect is finally removed by increasing the calcination temperature, whereas the surface trapping sites (Ti^{3+} or O^-) are more formed.

1-4. Photoluminescence Study: the Evidence for the Formation of Surface Active Sites

Photoluminescence spectra measured at 77 K for titania particles prepared by the sol-gel method and calcined at 500 °C are shown in Fig. 7. A single peak around 540 nm was obtained. According to Anpo's report on the photoluminescence of titania [Anpo et al., 1985], a high intense photoluminescence is observed when titania is highly dispersed on vycor glass. The peak point in titania anchored on vycor glass was around 440 nm. Anpo et al. also reported that bulk titania shows a photoluminescence spectrum around 450-550 nm [Anpo et al., 1989]. This result is similar with our obtained photoluminescence spectrum in Fig. 7. Therefore, we confirm that the obtained photoluminescence is due to the bulk anatase.

The peak intensity of photoluminescence is dependent on the kinds of species adsorbed on the surface of titania because it results from the recombination of photo-excited electron and hole pairs. Anpo et al. reported that the photoluminescence is quenched by the

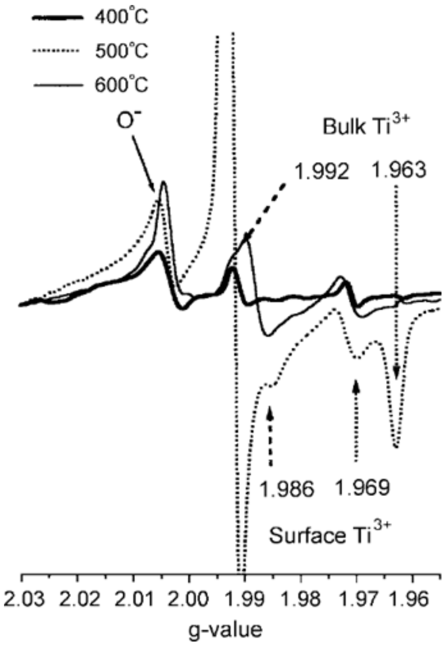


Fig. 6. EPR spectra measured at 77 K after the heat treatment at 300 °C under a vacuum condition for TiO_2 prepared by the sol-gel method.

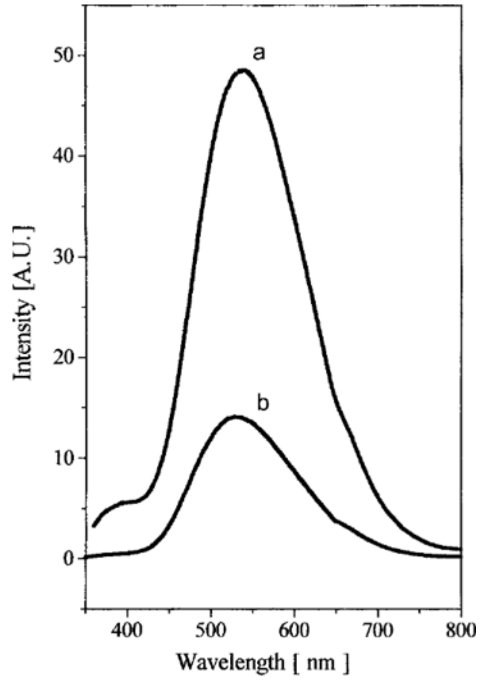


Fig. 7. Photoluminescence spectra measured at 77 K without (a) and with (b) 20 torr of oxygen for TiO_2 prepared by the sol-gel method.

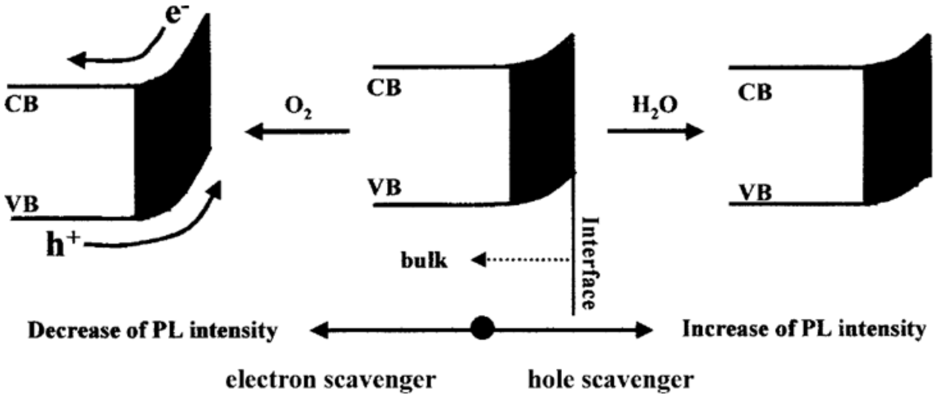


Fig. 8. Schematic diagram for the band bending in the space charge layer by the adsorbed species [Anpo et al., 1991].

addition of oxygen or improved by the water [Anpo et al., 1988, 1989]. They explained this quenching for enhancing of photoluminescence with the band bending as shown in Fig. 8. When the oxygen is adsorbed on the titania surface, the edge positions of conduction and balance band in the space charge layer are bent upward. As a result, the charge separation of photo-excited electron and hole pairs is facilitated and results in suppressing their recombination. On the contrary, the addition of water reduces the bend bending of conduction and valence bands in the space charge layer and accelerates the recombination of photo-excited electron and hole pairs. As a result, more efficient photoluminescence is achieved.

In this work, it is tried to estimate the relative quantity of surface active by calculating the difference in the intensity of photoluminescence measured before and after 20 torr of oxygen is added as shown in Fig. 7. The difference in the intensity of photoluminescence with and without the oxygen results from the interaction between the surface active sites and the added oxygen. For all titania samples prepared by the sol-gel method, photoluminescence quenching with 20 torr of oxygen was carried out. The difference in the intensity of photoluminescence obtained with and without the oxygen is shown in Fig. 9. The quenched intensities of photoluminescence for the sol-gel derived titania particles increase as the calcination temperature increases. This result says that more surface active sites are produced by increasing the calcination temperature. One should notice that the photoactivity of titania is also increased as the calcination temperature increases up to 600 °C as shown in Fig. 2. Therefore, it is clear that the increase of photoactivity for sol-gel driven titania particles with increasing the calcination temperature is due to the formation of surface trapping sites as well as the increase of crystallinity.

2. Photoactivity of Titania-Based Mixed Oxides

2-1. Improved Thermal Stability of Anatase Phase and Enhancement of Photoactivity

Fig. 10 shows the XRD results of 10-silica/titania mixed oxide prepared by the sol-gel method. Different from pure titania, in which the rutile phase was formed at 600 °C, 10-silica/titania mixed oxide has pure anatase phase at all calcination temperatures ranging from 500 to 800 °C. This high temperature heat treatment makes the prepared silica/titania mixed oxide of high crystallinity.

The photoactivity of 10-silica/titania mixed oxide is shown in Fig. 11 with pure titania for several calcination temperatures. The photoactivity of 10-silica/titania mixed oxide calcined at 700 and 800 °C is higher than that of pure titania calcined at 500 and 600 °C. Form this result, we confirm that higher temperature heat treatment leads higher photoactivity as long as no significant rutile phase

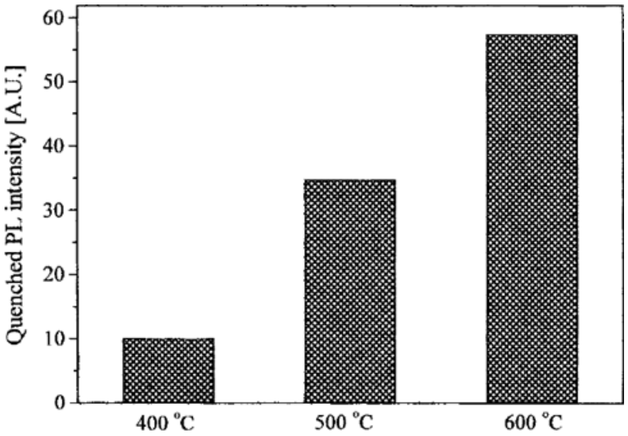


Fig. 9. Quenching intensity of TiO_2 prepared by the sol-gel method for several calcination temperatures.

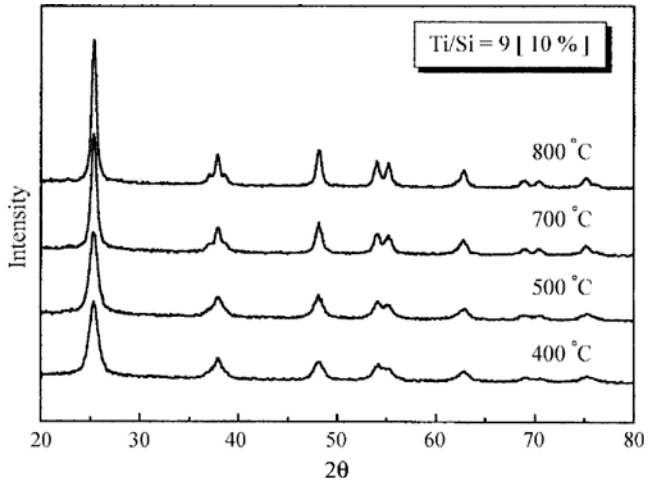


Fig. 10. XRD results of SiO_2/TiO_2 mixed oxides prepared by the sol-gel method for several calcination temperatures.

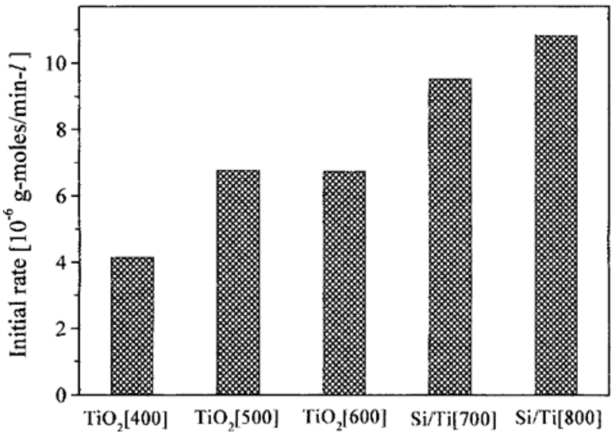


Fig. 11. Initial rates for the decomposition of TCE of TiO_2 and SiO_2/TiO_2 prepared by the sol-gel method: In TiO_2 [X] or Si/Ti[X], X means the calcination temperature.

is formed.

The surface area is also important for the improvement of photoactivity. The surface area of 10-silica/titania mixed oxide calcined at 800 °C is 77.4 m^2/g, whereas, pure titania calcined at 600 °C is 23.5 m^2/g. This higher surface area of 10-silica/titania mixed oxide is one reason for the improved photoactivity. Therefore, it is expected that the simultaneous increase of the crystallinity and the surface area could improve the photoactivity further more.

2-2. Simultaneous Increase in the Surface Area and the Crystallinity

In this work, we tried to increase both the crystallinity and the surface area in order to increase the photoactivity. From the XRD analysis, no rutile phase is found in all silica/titania samples calcined at 800 °C. Fig. 12 shows the surface area and the photoactivity of silica/titania mixed oxide. The surface area of silica/titania mixed oxides increases with increasing the content of silica with respect to titania. The photoactivity (g-mole/min-l) of silica/titania mixed oxides is also greatly improved with compared to that of pure titania. The photoactivity of silica/titania mixed oxide shows a maximum at 30% of silica, whereas the surface area is monotonically increased as the silica content increases.

In general, silica does not have photocatalytic activity. The silica in silica/titania mixed oxide plays two important roles to improve the photoactivity: to enhance the thermal stability of titania and to supply adsorption sites to the electron or hole consumers. The former was already identified from the XRD result. The latter role is not clear in this work. According to the analysis of FT-IR, the surface OH groups are produced more and more as the silica content increases. The increase of surface OH groups by adding the silica is an indirect evidence that the silica supplies the adsorption sites of reaction intermediates because it is well known that the OH groups are a primary consumer of photo-excited holes.

Above 30% of silica, although the surface area is increased, the reduction of photoactivity is because the increase of surface area does not compensate the reduction of titanium atoms, which are active sites. The photoactivity per the used titania (g-moles/min-gTiO_2) is shown in Fig. 13. The photoactivity is monotonically increased with increasing the silica content. The surface coverage of silica in silica/titania mixed oxide increases with increasing the silica content. Considering that photocatalysis is taking place on the surface, an increase in the surface coverage of silica more than a limit may be not good for the improvement of photoactivity because only titania can observe the UV light used in this work and produce electron and hole pairs. Therefore, there is an optimal composition of silica with respect to titania.

2-3. Removal of Bulk Ti^{3+} and Formation of New Surface Active Sites for Silica/Titania Mixed Oxide

The objective of using the silica is to enhance the thermal stability of titania. The increased thermal stability makes it possible to increase the crystallinity of prepared photocatalyst by high temperature heat treatment without rutile formation. The major effect of high temperature heat treatment is to reduce bulk defects. In order to see the existence of Ti^{3+} in silica/titania mixed oxide, EPR measurement was carried out. Fig. 14 shows EPR spectra measured at 77 K for 30-silica/titania mixed oxide. No peak assigning Ti^{3+} is

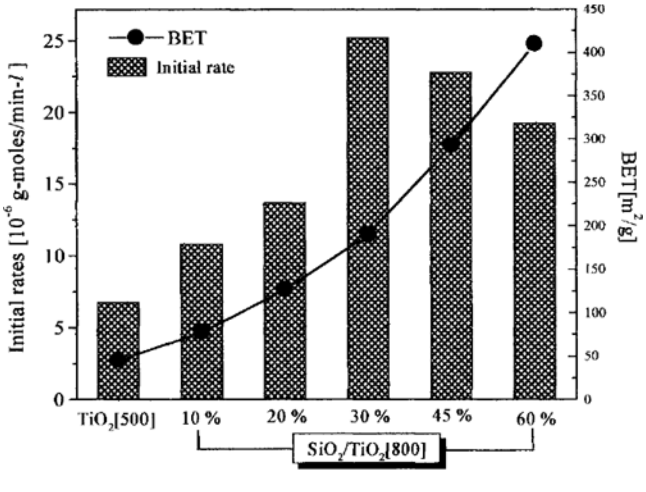


Fig. 12. Photoactivity and BET surface area of TiO_2 and SiO_2/TiO_2: In TiO_2 [X] and SiO_2/TiO_2 [X] means the calcination temperature. The percentage in the bottom of x-axis is the content of silica with respect to titania.

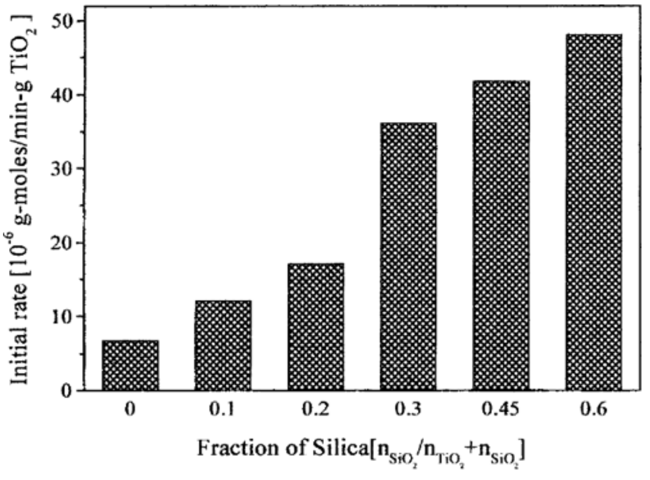


Fig. 13. Photoactivity in moles of TCE decomposed per unit time and unit TiO_2 used for silica/titania mixed oxides prepared by the sol-gel and calcined at 800 °C as a function of the silica content.

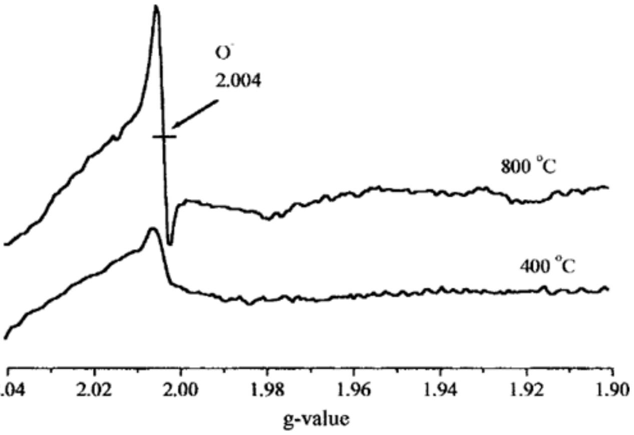


Fig. 14. EPR spectra measured at 77 K for 30-silica/titania mixed oxide.

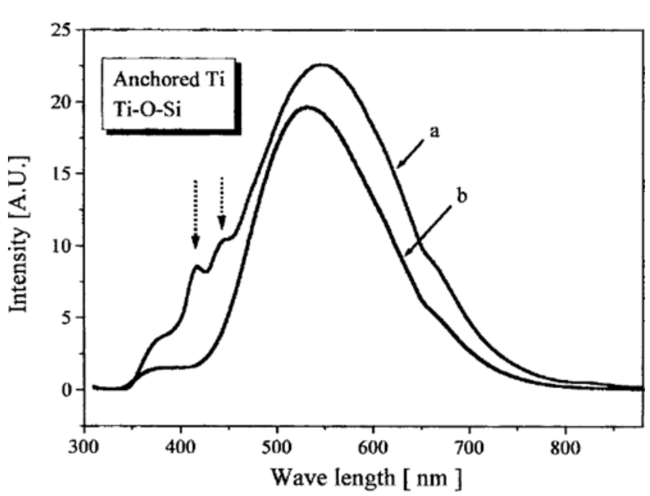


Fig. 15. Photoluminescence spectra measured at 77 K without (a) with (b) 20 torr of oxygen for 30-silica/titania mixed oxide.

observed. whereas the peak for O^- appears at both samples calcined at 400 and 800 °C, respectively. The peak intensity of O^- species is also increased by increasing the calcination temperature from 400 to 800 °C. This result is the same as that of pure titania: the increase of calcination temperature produces surface active sites. From this result, it is found that the addition of silica suppresses the formation of Ti^{3+} defect sites. As a result, a great improvement of photoactivity was achieved.

The photoluminescence spectra of 30-silica/titania mixed oxide are shown in Fig. 15. In the difference with pure titania as shown in Fig. 9, two new shoulder peaks(which are denoted by anchored Ti in Fig. 15) in the spectrum measured without oxygen at 77 K appear in the case of silica/titania mixed oxide. The peak around 500 to 510 nm is for the bulk titania [Anpo et al., 1989]. But, the shoulder peaks around 400 to 480 nm are not for bulk titania. Referring to the literature [Anpo et al., 1985; Marchese et al., 1997; Zhang et al., 1998], these shoulder peaks are atttributed to the anchored titanium, thus Ti-O-Si bond. The existence of Ti-O-Si bond is confirmed by FT-IR spectra. A more interesting result is that these peaks for anchored titania are completely quenched by the oxygen of 20 torr. This result means the Ti-O-Si bonds existing on the surface of silica/titania mixed oxides are very active sites which could easily interact with oxygen which is a major electron consumer.

2-4. Importance of Surface OH Groups for the Positive Effect of the Thermal Stabilizer on the Photoactivity

The key concept for improving the photoactivity is to increase the crystallinity of anatase titania by high temperature heat treatment without the accompanying formation of rutile phase. As mentioned previously, the use of silica as a thermal stabilizer of titania was successful to improve the photoactivity by enhancing the thermal stability of titania, which suppresses the phase transition from anatase to rutile even though the calcination temperature is over 700 °C. Then, it is expected that the photoactivity could be improved by using the secondary metal oxides if they act as a thermal stabilizer of titania. In this work, zirconia and alumina are used as a thermal stabilizer like silica.

Fig. 16 shows XRD results and the photocatalytic activity of zirconia/titania mixed oxides. The content of zirconia with respect to titania is 10 at.%. No rutile phase is observed at all calcination temperatures. Therefore, the zirconia added successfully improves the

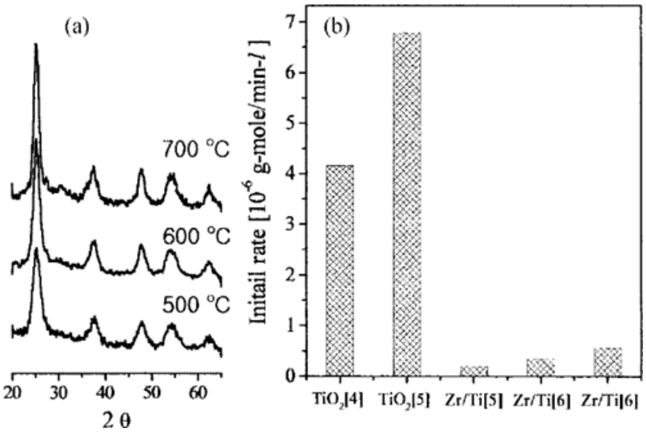


Fig. 16. XRD (a) and photocatalytic activity (b) titania and 10-zirconia/titania mixed oxide. In TiO_2 [X] and Zr/Ti [X], X means the calcination temperature. For example, TiO_2 [5] is titania calcined at 500 °C.

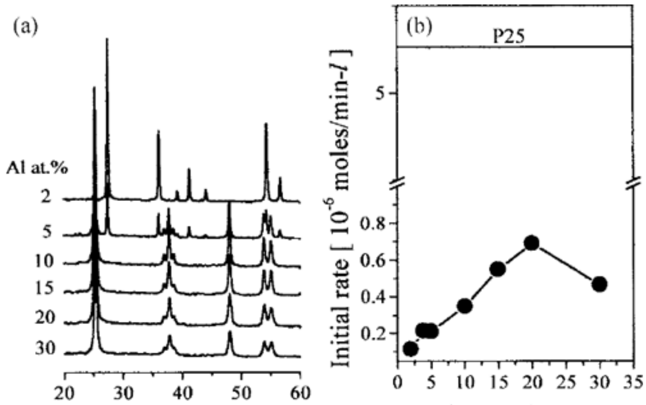


Fig. 17. XRD (a) and photocatalytic activity (b) of titania and alumina/titania mixed oxide calcined at 800 °C.

thermal stability of titania. The photoactivity of zirconia/titania mixed oxides, however, is not improved as shown in Fig. 16(b). The surface area of zirconia/titania calcined at 700 °C is 58.7 m^2/g. Nevertheless, the photoactivity of zirconia/titania mixed oxide is not greater than that of pure titania which is calcined at 500 °C and has a surface area of 45.9 m^2/g.

The XRD spectra of alumina/titania mixed oxides calcined at 800 °C are shown in Fig. 17(a) for the varied content of alumina. When the content of alumina was less than 10%, a significant rutile phase was formed. However, no rutile phase is formed as the content of alumina is varied from 10 to 30 at.%. At a fixed composition of zirconia to titania, the photoactivity was increased with increasing the calcination temperature as long as rutile phase was not formed. For alumina/titania mixed oxides, the maximal photoactivity obtainable at each composition is shown in Fig. 17(b). In the same manner as zirconia, the photoactivity of alumina/titania mixed oxides is not improved compared to pure titania. The loss of surface area as increasing the calcination temperature is not responsible for the low photoactivity of alumina/titania mixed oxide because the surface area of 20-zirconia/titania mixed oxide calcined at 800 °C is 48.2 m^2/g.

From the result of zirconia/titania and alumina/titania mixed oxides for the photoactivity, it is clear that the only enhancement of thermal stability by embedding the secondary metal oxide into titania matrix does not improve the photoactivity. Then, it is speculated that some other factor as well as the increase of thermal stability should be satisfied in order to achieve the improved photoactivity when titania is modified by the second metal oxide. Fig. 18 show FT-IR spectra of titania, 30-silica/titaniai, 10-zirconia/titania, and 20-alumina/titania mixed oxides. Pure titania and silica/titania mixed oxide has many surface OH groups, whereas, zirconia/titania and alumina/titania mixed oxide has little surface OH groups. Therefore, we conclude that the other condition for improving the photoactivity of titania by using the second metal oxide is the increase of surface OH groups.

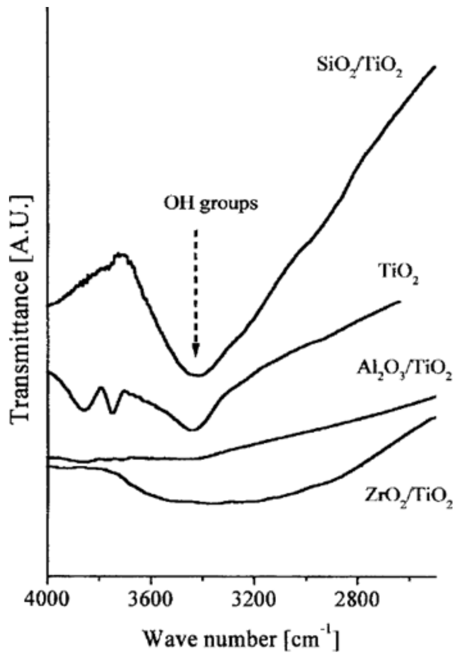


Fig. 18. FT-IR spectra of TiO_2 calcined at 500 °C, SiO_2/TiO_2, ZrO_2/TiO_2, and Al_2O_3/TiO_2 mixed oxides prepared by the sol-gel method and calcined at 800 °C.

CONCLUSIONS

Titania, silica/titania, zirconia/titania, and alumina/titania mixed oxide were prepared by the sol-gel method and their photocatalytic activity was investigated. It was reconfirmed that higher temperature heat treatment leads to higher photoactivity. It was found that the photoactivity of titania has a linear relationship to the crystallite size of anatase phase. From EPR analysis for pure titania, it was found that the bulk defect is removed by elevating the calcination temperature and the surface defect such as O^- is formed furthermore. According to the analysis of photoluminescence, the surface of titania turns out to be more active by the post heat treatment. Therefore, we concluded that the increase of photoactivity as the calcination temperature increases is due to the formation of surface active sites such as O^- as well as the increase of crystallinity resulting from the reduction of bulk defect.

In the investigation of the photoactivity of silica/titania mixed oxide, we concluded that the improvement of the thermal stability of anatase phase made it possible to enhance the photoactivity of titania because the prepared catalyst was calcined at a higher temperature than 700 °C without forming rutile phase. Also, the photoactivity was greatly improved by simultaneously increasing the surface area and the crystallinity as the content of silica increases up to 60%. By the analysis of EPR and photoluminescence, it was found that the embedding of silica into titania matrix suppressed the formation of Ti^{3+} and produced a new active site of Ti-O-Si, which easily interacts with the oxygen.

From the investigation of the photoactivity of zirconia/titania and alumina/titania mixed oxide, it was found that only an increase of thermal stability of anatase phase does not lead to the enhancement of photoactivity. To positively affect the improved thermal stability on the photoactivity, it was essential to increase the surface OH groups together.

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