Surface Structure and Photocatalytic Activity of Ti Supported on Alumina Powder†

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Abstract

Surface modified alumina powder that has photocatalytic activity was studied. To control the amount of Ti introduced on the surface at the molecular level, the powder was prepared by chemical surface modification with a monofunctional titanate-based coupling agent, followed by partial oxidation of the modification group. The surface density of Ti introduced onto the surface was quantitatively increased with the concentration of the modifying reagent, and/or repetition of the modification. Furthermore, the relationship between the surface structure and the occurrence of photocatalytic activity was examined. The surface structure was measured by XPS and UV-Visible absorption spectrometry. The photocatalytic activity was determined by measuring the degradation of Methylene Blue molecules in water solution with UV irradiation. Photocatalytic activity was realized at a Ti surface density of 3.7 nm−2. The optical absorption edge in UV of the sample shifted to longer wavelengths. The ability as a photocatalyst increased with the amount of Ti-O-Ti. Photocatalytic activity was recognized to be related to the amount of Ti-O-Ti on the alumina surface and the ability of UV absorption.

Key words: Alumina powder, Photocatalyst, Photodegradation, Surface modification, Titanate-based coupling agent

1. Introduction

TiO2 of anatase type is a typical photocatalyst that is capable of degrading contaminants with the aid of sunlight or artificial illumination without requiring demanding conditions such as high temperature or high pressure. For this reason, this substance is now expected to be used in diverse industrial fields1). In particular, there is a strong demand for adoption of the substance to address environmental issues. Accordingly, many reports are available about its degradation mechanism with organic pollutants2-6) and development of a highly active photocatalyst7-8). For development of a highly active photocatalyst, much research about binary metal oxides has already been carried out. As early as 1985, Kakuta et al. reported that the photocatalytic activity of ZnS-CdS/SiO2 excels in comparison to that of ZnS/SiO2 or CdS/SiO2 compounds9). Recently, Anderson et al., Fu et al., Yu et al., Do et al. and Papp et al. have investigated the photocatalytic activity of TiO2/SiO2, TiO2/Al2O3, TiO2/ZrO2, TiO2/WO3, and TiO2/MoO3 systems10-14). These researchers demonstrated that enhanced photocatalytic activity is obtainable with a binary metal oxide system.

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Focusing on alumina as a base material, the authors researched the possibility of using it as a photocatalyst. Due to its basic characteristics, including high hardness, heat resistance and chemical resistance, alumina is commonly used as an industrial material. Expanding the functionality of this substance will produce much applicability of the substance. Anderson et al., in their research into TiO$_2$/Al$_2$O$_3$ photocatalysts prepared by a sol-gel process, reported on the effects of the TiO$_2$/Al$_2$O$_3$ ratio, TiO$_2$ region size within particles and adsorption on the photocatalytic activity of TiO$_2$/Al$_2$O$_3$. Incidentally, the photocatalytic activity of binary metal oxides is strongly governed by the conditions of presence and surface structure of TiO$_2$; these two factors greatly affect whether or not TiO$_2$ can function as a photocatalyst. For TiO$_2$/SiO$_2$ systems, this tendency was studied with a CVD process$^{15}$, an ion injection process$^{16}$ and a surface modification process$^{17}$. However, a similar study was still lacking for TiO$_2$/Al$_2$O$_3$ systems. To address this issue, the authors have attempted atomic level surface design for alumina powder by employing a surface modification processes in order to allow TiO$_2$ to be supported on Al$_2$O$_3$. With this technique, the authors introduced Ti atoms onto the surface of alumina particles (the base material) to increase gradually Ti sites on the alumina particles, thereby transforming Al$_2$O$_3$ into a photocatalyst. XPS measurements, UV absorption edge measurements, and Methylen Blue degradation tests were measured to evaluate the properties of the prepared samples at every stage of the procedure. The relationship between the surface structure of the prepared samples, especially the Ti-supporting state, and the photocatalysis expression mechanism with the supported Ti was discussed.

2. Experimental

2.1 Sample preparation

Fine alumina powder (aluminum oxide C; Nippon Aerosil) was used as the base material, while the modifier used to introduce Ti was isopropyltriisostearoyltitanate (CH$_3$)$_2$CHO-Ti-(OCOC$_{17}$H$_{35}$)$_3$ (KEN-REACT KKR-TTS; Kenrich Petro-chemicals Co.). The molecule of this modifier includes three stearoyl groups as hydrophobic side-chain organic functional groups and one hydrophilic hydrolytic degradable group. For this reason, the single modifier reacts with a hydroxyl group on the surface of the alumina particles without polymerization among modifiers. At the same time, owing to steric hindrance with the stearoyl groups, individual Ti atoms appeared to exist on the surface of the alumina particles, separated from each other at a regular specific distance between the atoms$^{17-19}$. In order for these features to be utilized for accurate surface design of alumina powder, the authors chose the above-mentioned modifier.

Introduction of Ti was achieved through a process comprised of chemical surface modification and organic chain combustion by oxidation. First, alumina was added in a modifier solution using n-hexane (analytical grade; Kanto Kagaku) as a solvent, and then surface modification was performed through the reflux method to introduce the modifier group onto the surface of the alumina particles. Next, the sample was filtered off under increased pressure, rinsed with n-hexane, and oxidized by combustion with flowing oxygen to remove the organic chains (stearoyl groups) in the modifier group. This process, comprised of chemical surface modification and organic chain combustion by oxidation, was taken as one modification procedure, and this procedure was repeated eight times in order to prepare nine samples that included one unmodified (original) alumina and eight alumina samples that underwent the modification procedure from one to eight times.

For surface modification, the saturation modification-capable conditions were investigated in advance, and 12 g of alumina powder and 12 g of modifier (at saturation modification conditions) were added to 830 mL of n-hexane and the mixture was refluxed for 1 hour at the boiling point of hexane. Pressure filtration and rinsing were performed with a membrane filter of pore diameter 0.1 μm (Type JV; Nihon Millipore) at a pressure of 5 kgf/cm$^2$. Note that the modified samples were thoroughly rinsed with hexane in order to remove any unreacted modifier (modifier that had been physically adsorbed). Combustion by oxidation was achieved in 10 hours at 450°C with oxygen supplied at a rate of 500 mL/min by an electric furnace (Super Burn; Motoyama). The removal of unreacted modifier by rinsing and burning of organic chains through combustion by oxidation is a particularly important step in ensuring accurate particle surface design. Therefore, the modification procedure was started only after determining the relevant requirements for the necessary rinsing thoroughness, and the temperature and duration of combustion. The necessary rinsing thoroughness was determined based on the trend in weight decrease of the modifier as a result of combustion by using the TG-DTA described below. The rinsing step was repeated until variation in the weight of the modifier was no longer detected and this was taken as the rinsing thorough-
mass point at which unreacted modifier was satisfactorily removed. Note also that combustion by oxidation was attempted only after determining the temperature and duration at which the organic chains in the modifier could be oxidized and removed, by adopting the FT-IR technique.

2.2 Evaluation of physical properties

For estimation of the introduced Ti on the prepared samples, TG-DTA (Thermo Plus; Rigaku Denki) was used. The samples that had not yet undergone combustion by oxidation were subjected to this test; thereby quantification was achieved based on the decrease in weight resulting from combustion of the organic chains. In addition, the physical properties of the samples were evaluated by subjecting the samples to specific surface area measurements, verification of structural variation by using XRD (MX Labo 2; Bunker AXS), observation of fine particle surfaces using TEM (JEM-2000FX; JEOL), analysis of the state of electrons on the surfaces of particles using XPS (ESCA3400; Shimadzu), UV absorption edge measurement, and evaluation for photocatalytic activity. Specific surface area measurement was performed by the nitrogen adsorption method using the GEMINI2360 (Shimadzu). The UV absorption edge of the samples was measured with a UV visible spectrophotometer (UV-3100C; Shimadzu) through diffuse reflectance spectroscopy. The photocatalyst function of the samples was evaluated based on their Methylene Blue (MB) degradation activity. The amount of Methylene Blue degraded was measured by using a UV visible spectrophotometer (U-3210; Hitachi), wherein 0.1 g of sample was added to 25 mL of aqueous Methylene Blue solution whose concentration was 2.0×10^{-5} mol/L. The mixture was irradiated with UV rays for 6 hours while being stirred. Then the solution was filtered off from the suspension and the degree of degradation was analyzed. For filtration of the suspension, a membrane filter of pore diameter 0.2 µm (Type LG; Nihon Millipore) was used. For irradiation with UV rays, two 6 W UV lamps (Black Light; Matsushita Electric Industrial Co., Ltd.) with wavelength ranges of 300 to 400 nm (peak wavelength 352 nm) were used.

3. Results

3.1 Determination of the amount of Ti introduced

Determination of the amount of Ti introduced is graphically plotted in Figure 1. As the modification procedure of chemical surface modification and organic chain combustion by oxidation was repeated, roughly the same amount of Ti was introduced each repetition, although the amount introduced somewhat decreased as the number of repetitions increased. More specifically, an average of 0.6 atoms/nm² of Ti was introduced onto the alumina surface each modification procedure repetition, with a total of approximately 4.7 atoms/nm² of Ti introduced through eight repetitions. In summary, it was understood that the introduction of Ti atoms onto the surface of alumina particles can be quantitatively controlled.

3.2 Effect of transformation into a photocatalyst on surface and bulk structure

As a result of specific surface area measurements, it was understood that the BET specific surface area of untreated alumina powder was 107.8 m²/g, while that of the sample that underwent eight repetitions of the modification procedure was 108.6 m²/g. In other words, there was no significant change in the specific surface area due to transformation into a photocatalyst. In addition, from this result, it was also apparent that micro surface sintering (that is, change in the surface structure of alumina particles) did not occur as a result of the combustion by oxidation process at 450°C.

Next, the XRD patterns of each sample are illustrated in Figure 2. The crystal structure of the untreated sample consisted predominantly of δ-alumina. There was no significant variation in the XRD pattern among the samples, from the untreated one to the eight-repetition one. Consequently, it was understood...
that repetition of the modification procedure does not significantly affect the crystallinity or crystal structure of the alumina. Incidentally, no XRD pattern associated with TiO$_2$ (anatase, rutile, brookite) was found.

TEM images of the untreated sample and the sample that underwent eight modification procedure repetitions are given in Figures 3A and 3B, respectively. The primary particle diameter of the alumina powder measured from 10 to 20 nm. There was no significant difference in the diameter of primary particles between the unmodified and modified samples. In the appearance, the difference such that finer particles attached on modified alumina particles wasn’t found between the unmodified and modified samples. In addition, no fine particles that appeared to be TiO$_2$ were observed on the modified samples.

The above results of specific surface area measurements, XRD measurements and TEM observations show that the proposed process of transformation into a photocatalyst test did not adversely affect the properties of the alumina as a base material.

### 3.3 Analysis of surface electron state by XPS

The Ti2p and O1s spectra for the samples are shown in Figures 4A and 4B, respectively. The Ti2p spectra in Fig. 4A shows that, as the modification procedure was repeated, the amount of introduced Ti increased and the peak shifted to a lower energy
level. For example, the Ti2p3/2 peak of the sample that underwent modification once occurred at 459.7 (eV), while the peak of the sample that underwent modification eight times was at 459.1 (eV). From this finding it seems that repeated modification caused titanium oxide clusters to occur on the surface of alumina particles and the Ti to eventually take the oxidation state of TiO2 (Ti2p3/2; 458.7 eV)\(^{19}\).

Next, with the O1s spectrum for untreated Al2O3 in Fig. 4B, the peak belonging to O1s is present at 531.8 eV. As the number of repetitions of the modification procedure increased, the O1s peak shifted to a lower energy level. The O1s peak of the sample that underwent modification eight times is found at 531.2 eV. This peak shift seems to result from the emergence of O1s belonging to -Ti-O- that was formed by the modification procedures. In other words, it seems that the proportion of alumina at the surface decreased while the proportion of -Ti-O- increased, and that, as a result, the O1s peak shifted to the lower energy level of the O1s of TiO2 (529.9 eV)\(^{19}\). In summary, because of being gradually covered with titanium oxide as the modification procedure was repeated, the surface of the alumina particles seemed increasingly to take on the surface state of TiO2.

3.4 Result of UV absorption edge measurement

The results of the measurements of the UV absorption edge are shown in Figure 5. Virtually no UV absorption was found with the untreated alumina. However, for the sample that underwent the modification procedure once, minor UV absorption was detected for shorter wavelengths, relative to the absorption of TiO2 (anatase). As the number of repetitions of the modification procedure increased, the UV absorbance gradually increased and the UV absorption edge shifted to relatively longer wavelengths. The magnitude of the absorption edge shift per modification procedure repetition, however, decreased as the number of repetitions increased.

3.5 Evaluation of photocatalytic activity

Figure 6 shows the change of Methylene Blue concentration as an index of the photocatalytic activity. Decreases in Methylene Blue concentrations in the samples not irradiated with UV were from adsorption of Methylene Blue onto the surface of the samples. The amount of adsorption did not differ significantly between the unmodified sample and the samples subjected to the modification procedure for one to eight repetitions. Three possible causes for the decrease in Methylene Blue concentration in the samples not subjected to UV irradiation are adsorption, photocatalytic degradation, and direct degradation of Methylene Blue by normal UV exposure. As is clear in Fig. 6, among the samples irradiated with UV, those having undergone the modification procedure six or more times exhibited significant decreases in Methylene Blue concentration. As mentioned previously, there was no significant variation in the amount of adsorbed Methylene Blue, and the effectiveness of direct degradation of Methylene Blue by normal UV exposure appears to be constant regardless of whether the sample is modified or not. In summary, the authors have verified that photocatalytic action is achieved by repeating the modification procedure six or more times.
times under the authors’ test conditions, resulting in the total introduction of at least 3.7 atoms/nm² Ti from the modification procedure repetitions. The photocatalytic action intensified as the Ti amount introduced increased.

4. Discussion

4.1 Change in alumina surface structure and hydroxyl group number

From the measurement results obtained with the Grignard reagent method, the number of hydroxyl groups on the surface of untreated alumina was approximately 7.07 groups/nm². It is apparent that a sufficiently large number of reaction sites were present compared with the number of Ti atoms (0.69 atoms/nm²) introduced as a result of the first modification procedure. From the feature of the proposed modification technique, every Ti atom appears to have been introduced onto the surface of alumina particles as a result of the first modification procedure, with the Ti atoms being spaced a specific regular distance apart from each other. Assuming that three hydroxyl groups occur on Ti atoms as a result of removal of organic chains by oxidation, the total number of hydroxyl groups on each alumina particle will increase by 1.38 groups/nm² because of the decrease in Al-OH groups and the formation of Ti-OH groups on the reaction sites. Accordingly, the number of hydroxyl groups is calculated as 7.07 + 1.38 = 8.45 groups/nm². Under this assumption, the number of Al-OH groups after the first modification procedure is 6.38 groups/nm² and the number of Ti-OH groups is 2.07 groups/nm², making the ratio of Al-OH groups to Ti-OH groups approximately 3:1. However, the measured value of the surface hydroxyl groups in the sample after the first modification procedure was 6.75 groups/nm². The presumed cause for why the number of surface hydroxyl groups in the sample after the first modification procedure was smaller than the calculated value is dehydration condensation between Al-OH and Al-OH as well as between Al-OH and Ti-OH.

As a result of the second modification procedure repetition onwards, the modifier was introduced not only to the existing Al-OH groups but also into the newly formed Ti-OH groups, thereby Ti-O-Ti bonds were formed. Apparently, the proportion of Ti-OH groups among the total number of surface hydroxyl groups increased and dehydration condensation occurred between Ti-OH and Ti-OH. Also, it is clear that the shift of O1s peak to a lower energy level, as shown in Fig. 4B, resulted from the increase of Ti-O-Ti bonds formed in the above two ways.

4.2 Surface structure of modified alumina and mechanism of photocatalysis

Because the modifier groups are introduced to the hydroxyl groups on the surface of alumina particles as a result of the first modification procedure, the Al-O-Ti bonds occur on the surface of alumina particles. Hydroxyl groups appear to exist on the introduced Ti after combustion of organic chains. As a result of the second modification procedure repetition onwards, modifier groups are introduced to the hydroxyl groups remaining on the surface of alumina particles and to the hydroxyl groups on the introduced Ti. Consequently, not only Al-O-Ti bonds but also Ti-O-Ti bonds seem to be formed. Note that Ti-O-Ti bonds are also formed as a result of dehydration condensation of hydroxyl groups on Ti. However, as described earlier, because each Ti atom is introduced separated from other Ti atoms at a specific distance as a result of the first modification procedure, the hydroxyl groups on each Ti do not seem to dehydrate and form Ti-O-Ti bonds. Ti-O-Ti bonds seem to have formed from repetition of the modification procedure, as well as through the growth of the so-formed Ti-O-Ti bonds, and this caused the UV absorption edge to shift to the red end of the spectrum. The expansion of the range of absorbable wavelengths resulting from this “red shift” of the UV absorption edge appears to contribute to the expression of photocatalytic activity.

5. Conclusion

The procedure to introduce Ti onto the surface of alumina particles with their surface modification technique was investigated. The surface structure, physical properties, and the photocatalytic activity of the prepared samples were discussed, and reached the following conclusions:

1) Introduction of Ti onto the surface of alumina particles by surface modification techniques can be quantitatively controlled with the concentration of the modifier and/or the number of modification procedure repetitions.
2) The process for transformation into a photocatalyst (chemical surface modification and organic chain combustion by oxidation) does not significantly affect the bulk structure and characteristics of alumina.
3) As the modification procedure was repeated, Ti-O-Ti bonds occurred on the surface of alumina particles, and, at the same time, the UV absorption made
red shift. The oxidation state of Ti seemed to resemble that of the Ti in titanium oxide.

4) By introducing a total of 3.7 atoms/nm² Ti with six modification procedure repetitions, the alumina achieved photocatalytic activity. It was considered that the appearance of photocatalytic activity related with the increased amount of photons being absorbed due to the shift of the absorption edge to the red.

Appendix

Several interesting results were found out after the related studies have been done. Here, I introduce a few of them as a supplement. Two kinds of photocatalyst based on CaCO₃ and SiO₂ were prepared using the same procedure of Al₂O₃ as I mentioned in this paper. One of the studies, photocatalyst based on CaCO₃ showed almost the same results of Al₂O₃, in other word, the photocatalytic activity appeared after the formation of titania-like layer on the surface of CaCO₃. On the other hand, the result of photocatalyst based on SiO₂ was totally different from that of Al₂O₃ and CaCO₃. Although the sample treated by only one procedure had no Ti-O-Ti structures but Si-O-Ti structures, photocatalytic activity was occurred on the sample of SiO₂. A similar result was also obtained from other silicate materials.

References

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