Abstract

This paper is intended for the development of new photocatalyst composite materials by forming numerous fine projections on a substrate surface using magnetic fields and composite plating and by compositing titanium oxide on increased surface area via that method. Aspects from methods of producing materials to removal of hazardous gases using the materials produced have been studied in detail. Moreover, this paper reports tactics to improve the photocatalytic activity through feedback of results into sample production and study results with a view to practical application.

In recent years, high magnetic fields on the order of 10T have become relatively easy to use with the spread of superconducting magnets. Various magnetic field effects have been reported. Ferromagnetic particles such as nickel are arranged along lines of magnetic force; in keeping this state, deposition of metallic crystals by plating results in the deposited metallic crystals becoming a binder, allowing fixation of the aligned particles.

However, a photocatalytic reaction occurs on a titanium oxide surface, so fixation of titanium oxide onto a base material and creation of a large surface area are significant for its use in decomposition/removal of airborne contaminants. Materials obtained using this method, have a substantially increased surface area, so if titanium oxide on the surface can be composited, then this material can contact air pollutants effectively.

In this paper, methods of producing materials in magnetic fields were reported firstly. As an application, photocatalytic activities were evaluated by removal of nitrogen oxides, which was one of serious air pollutants in an urban area. Evaluation method of removal of nitrogen oxides had been established as a Japanese Industrial Standard (JIS). Then, removal of ethylene oxide which was released in the atmosphere in high concentrations was studied. Emission of ethylene oxides is not regulated legally, in spite of its highly hazardous and explosive property. It is expected to produce various by-products, so these by-products were also studied in detail.

This paper consists of eight chapters. The first chapter is an introduction and the eighth is a summary. An overview of the second through seventh chapters is as follows:

Chapter 2 describes, with regard to titanium oxide photocatalysts, the principle of photocatalytic activity for titanium oxides, fixation methods of titanium oxides and the decomposition of pollutants using photocatalysts, and recent researches about photocatalysts.

Chapter 3 describes about composite plating in the preceding part, and about magnetic fields and magnetic fields effects in the latter part.

Chapter 4 describes sample production. When nickel particles are spread over a copper plate and a magnetic field was imposed on them, the nickel particles align along lines of magnetic force; if the magnetic field is kept on imposition to them and electroplating is performed using copper sulfate solution, the deposited copper crystals become a binder. The nickel particles are fixed, and samples with numerous columnar projections vertical to the base material is obtained. A composite plating method is used to fix titanium oxide photocatalysts on this material surface. First, results of studying conditions for formation of projections indicated that projections were finer with a larger magnetic flux density and that the numerical density of projections rose. At this time, the surface area of the sample increased up to about 800 fold with respect to the bottom of the base material. Next, magnetic flux density, current density, and titanium oxide concentration in a plating bath were changed, and the composite ratio of

titanium oxide in the sample was measured. Titanium oxide composition grew with a lower magnetic flux density, and there was almost no compositing in the high magnetic field. To examine the causes of these phenomena, the solution was first stirred mechanically in no magnetic field, and the relationship between stirring intensity and the titanium oxide composite ratio was examined. Next, the positional relationship of the electrodes and magnetic field was changed, and the composite ratio of titanium oxide was measured under conditions which MHD flow would not generate. In addition, titanium oxide particles attached to electrodes are not readily retained because of the smoothed deposition surface due to the micro-MHD flow in a high magnetic field, so the cause is considered to be the MHD flow promoting detachment of titanium oxide adsorbed on the electrode surface.

Thus, the method of production was modified to form fine projections and increase the surface area while simultaneously compositing more titanium oxide on the surface of projections formed. The work succeeded in compositing titanium oxide on a surface with fine projections by changing the method of projection formation and titanium oxide composition from the previous single process to two processes, one in which fine projections were formed in a high magnetic field and another in which titanium oxide composition was performed in no magnetic field.

Chapter 5 describes evaluation of photocatalytic activities of produced materials through removal of nitrogen oxides. Nitrogen oxides refer to nitrogen monoxide and nitrogen dioxide. And almost of them are emitted as nitrogen monoxide. Nitrogen monoxide is converted into nitrogen dioxide in the atmosphere. Air quality standard regarding nitrogen dioxide have been set, and a reduction of concentration is required in urban areas. Removal of nitrogen oxides by use of titanium oxide photocatalyst has previously been studied in detail; last year, a method of evaluating the activity of photocatalyst was made into a Japanese Industrial Standard (JIS). Therefore, removal of nitrogen oxides was performed as a method of evaluating the activities of materials produced. Nitrogen oxides are oxidized to nitric acid on the titanium oxide surface and fixed to the sample, so the amount of nitrogen oxides removed can be measured by eluting it with ultra-pure water and quantifying it. Removal rates of nitrogen oxides for both flat samples and samples with projections were studied. With flat samples, the titanium oxide composition ratio and NOx removal rate was shown as a linear regression equation. The NOx removal rate for sample with projections, however, increased with the increase in the titanium oxide composition ratio at the top of projections, although removal activity was lower than that of flat sample. The reason for this result was that numerous projections generate a shadowed area when irradiated with ultraviolet rays, where the photocatalysts were not activated. To irradiate effectively with ultraviolet ray to the sides of projections and the bottom of the base material, modification of the method of irradiation was attempted. NOx Removal rates of samples with projections improved, although it failed to exceed the removal rates for flat samples.

Chapter 6 studied the decomposition and removal of ethylene oxide by use of the materials produced in chapter 4. Ethylene oxide used as a sterilizing gas in medical settings is highly toxic to humans and is also highly explosive. Nevertheless, it is emitted into the atmosphere in extremely high concentrations by small and medium-sized sterilization equipment, which accounts for the majority of such equipment, since there are no emissions regulations by law. In recent years, air quality standard in working environment have been set and processing technology verification tests have been conducted by the Ministry of the Environment, with regard to ethylene oxide processing equipment since 2003, so circumstances have changed dramatically.

Therefore, decomposition of ethylene oxide was attempted by use of materials produced. The initial concentration was 10 ppm and ultraviolet ray was irradiated with an 8W BLB-lamp; a maximum removal ratio of 72% was obtained in an hour. In addition, lamp with a curved mirror attached to the side in order to provide multifaceted irradiation with respect to projections resulted in the removal ratio improving to 85%. Evaluation of by-products during ethylene oxide decomposition was also done. Assuming the path of ethylene oxide decomposition, highly hazardous substances such as acetaldehyde and formaldehyde are generated as intermediates and may be released. In actuality, generation of these substances as part of the decomposition of ethylene oxide has been confirmed, so improvement in the removal ratio of ethylene oxide and suppression of aldehydes were studied. Multifaceted irradiation with respect to projections resulted in substantial suppression of the production of aldehydes. In order to estimate the major reaction path for the decomposition reaction, ultraviolet ray was irradiated to assumed intermediate products loaded on the sample. They can be quickly removed.

Chapter 7 reports on sample production using a neodymium magnet, which is a permanent magnet, and removal of nitrogen oxides using the materials produced. Previously, the materials were produced in a high magnetic field using a superconducting magnet, although if this can be replaced by a permanent magnet, then it offers an advantage in terms of cost in light of practical application. At the same time, large amounts of titanium oxides were not activated in samples with projections at a high numerical density.

This fact suggests the possibility that projections at a high numerical density are not needed. Therefore, sample production using a neodymium magnet, a powerful and relatively inexpensive permanent magnet, was studied. Lowering the magnetic flux density resulted in the surface area decreasing, and the numerical density of projections decreased. When samples were produced with a uniform magnet field of 0.45T using a neodymium magnet with 100 mm in a diameter, samples with a numerical density of 100-200 projections per cm^{-2} were obtained. The NOx removal rates of these samples increased to about 2 fold compared to those of flat samples and highly active samples with projections. This result can probably be considered insufficient activity compared to the substantial increase in the sample surface area by projections, although reducing the numerical density of projections to some extent would be effective in improving the activity of the materials. In addition, results suggest that use of a high magnetic field from a superconducting magnet is not necessarily needed. Significant results for practical application were obtained in terms of production costs and larger scale through a switch to a neodymium magnet, a permanent magnet.

Thus, this paper has reported a series of processes – production of new shapes, composition of a photocatalyst, decontamination of hazardous gases, and improvement of production method based on these results – with potential for development in each process. Results of these researches are not necessarily limited to photocatalysts and may be used in a variety of materials development or in the decontamination of hazardous gases.