学位論文内容の要旨

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学位論文題名

Studies on changes in surface/bulk structure and photocatalytic activity of titania powders induced by braying（磨砕による酸化チタン粉末の表面/バルク構造と光触媒活性の変化に関する研究）

For solid materials, characterization of their structures is not straightforward compared with that for molecules, i.e., both bulk and surface structures should be characterized. Moreover, solids are sometimes not crystalline, but amorphous part may be included. However, only bulk crystalline structure is describable, to be named reflecting its structure, e.g., anatase or rutile for titania samples. On the other hand, surface structures are indescribable, that is difficult to describe, since we have no systematic nomenclature method for solid surfaces except for single crystals exposing only one type of a facet. In addition, amorphous structures are also indescribable. In this sense, all the real solid samples have, at least partly, indescribable structures. In the long history of material-science studies, we have discussed without description of surface and amorphous structures even though those structures are included in them. However, the term "indescribable" does not mean intrinsically undescribable, that is impossible to describe, surface and amorphous structure are indescribable just because there are no practical methods for macroscopic surface analyses which provides the data reflecting the surface and amorphous structures of solid materials. In our laboratory, a novel method for solid material characterization, especially for semiconducting materials, reversed double-beam photoacoustic spectroscopy (RDB-PAS), has been developed, which could be benefit for filling up this gap about surface/amorphous-solids macroscopic analysis. The RDB-PAS is able to acquire patterns of energy-resolved distribution of electron traps (ERDTs)/conduction-band bottom (CBB) for various semiconducting metal oxides as a fingerprint and the ERDT pattern reflects surface structure of metal oxides. In this study, an attempt to reveal the changes in surface/bulk structure by braying and their influences on photocatalytic activities using RDB-PAS as well as conventional analyses such as X-ray diffraction (XRD) measurement. Here, three kinds of polymorphs of titanium(IV) oxide (titania) were used as starting materials and mechanical braying and post calcination at 773 K for 3 h was applied to change the surface/bulk structure of the samples.

In Chapter 1, the backgrounds of this study such as reported preparation methods and characterization methods for amorphous materials were introduced. Subsequently, the purpose of this study was mentioned.

In Chapter 2, preparation methods for amorphous titanias and characterization methods were introduced.

In Chapter 3, a commercial rutile titania was brayed for the period from 1 d to 10 d. The photocatalytic activities, evaluated in three systems of hydrogen evolution from deaerated aqueous methanol with in-situ photo-deposited platinum, carbon-dioxide evolution from aerobic aqueous acetic acid and oxygen evolution from water along with photodeposition of metallic silver, were drastically decreased by braying and could not be recovered completely by calcination, indicating braying changed the surface/bulk structure to result in the deactivations. However, negligible changes were measured by conventional analyses such as SEM analysis for the size and morphology of the particle and nitrogen absorption for specific surface area. On the other hand, XRD, X-ray diffractometry, measurement with nickel oxide as an internal standard revealed that the decreased rutile composition by braying was recovered by post calcination but the reduced crystallite size was not completely

recovered, which indicating a part, most probably surface, of rutile crystallites was amorphized by braying and almost recovered by post calcination for the samples brayed for < 5 d. For the longer-time brayed sample, amorphized surface layer could not be crystallized conformably with the core rutile to result in that independent small crystallites and amorphous layers, i.e., grain boundary, might remain between crystallites. In addition, ERDT analyses revealed that braying caused shift of main peak to higher energy side and a tailing peak at > 3.4 eV, in the position similar to the commercial amorphous titania, appeared for the samples brayed for > 2 d and decreased by post calcination, suggesting the surface amorphization by braying and recrystallization by post calcination. The deconvolution analyses of ERDT pattern with Gaussian-curve fitting, on the assumption of interparticle charge-transfer excitation, revealed that braying causes the surface amorphization to yield amorphous in contact with rutile (am-R) and post calcination partially recrystallizes into rutile. Longer-time braying thickens the depth of the surface amorphous layer to result in the formation of isolated amorphous (am). Recrystallization by post calcination induce lattice mismatch to leave uncrystallized amorphous components in contact with rutile, grain boundaries (am-R(GB)). Within the candidate's knowledge, this is the first example of direct measurement of three kinds of amorphous phases in the powder samples. Further long-time braying produces thicker amorphous layer to result in decomposition of particles into small pieces.

In Chapter 4, a commercial anatase titania sample was used as a starting material for braying and post calcination with the procedure same as for above-mentioned rutile samples. Similar to the case of rutile-based samples, braying induces the surface amorphization and recrystallization was induced upon post calcination, but the formation of grain-boundaries is limited to the long-time brayed samples. Therefore, the structure of short-time brayed-post calcined samples seem to be similar to original samples except for the presence of small amount of grain boundaries. In addition to those changes, crystalline-phase transition from anatase to rutile was also observed clearly in the change of XRD and ERDT/CBB patterns by braying and post calcination. Compared with the conventional crystalline phase-composition analysis by Rietveld XRD analysis, the RDB-PAS analysis, as a macroscopic surface analysis, might give clearer direct information on the surface structure of materials.

In Chapter 5, a commercial brookite titania sample was used as a starting material for braying and post calcination with the procedure same as for above-mentioned rutile and anatase-based samples. Distinguishing from the case of rutile and anatase, their ERDT/CBB-pattern analyses of the brookite-based samples suggested that the original sample was composed of a mixture of large secondary particles of brookite and amorphous. Therefore, braying might decompose those secondary particles gradually forming surface amorphous layers and post calcination induced the partial re-crystallization without giving appreciable grain boundaries to result in the slight decrease in their photocatalytic activity.

In the chapter of General Conclusions, the above-mentioned results and discussions on the samples of brayed/post-calcined rutile, anatase and brookite-based samples and their structure-photocatalytic activity correlation are summarized. By using ERDT/CBB patterns obtained by RDB-PAS, the changes in bulk/surface structure induced by braying and post calcination, at least three kinds of amorphous components in those samples, am, am-X and am-X(GB) (X: rutile, anatase or brookite) giving a little different influence on the activity of samples, were directly observed and the behavior of amorphization-recrystallization of titania samples could be characterized on the assumption of existence of different kinds of amorphous components. Thus, it can be claimed that ERDT/CBB analysis provided the information of amorphous components in titania samples. In other words, amorphous structure has now become describable. Change of structure of titania particles including amorphous has been clarified for the first time to interpret the change of photocatalytic activity. In the field of material science, we have ignored amorphous phase in the samples. The present results must open up new era of material design and characterization not limited to titania samples.