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Studies on interparticle charge-transfer excitation: Novel band-structure analysis of semiconducting metal-oxide photocatalysts based on energy-resolved distribution of electron traps

(粒子間電荷移動励起に関する研究－電子トラップ密度のエネルギー分布にもとづく半導体金属酸化物光触媒の新規バンド構造解析)

Metal oxides are widely used in large quantities as chemical/physical functional materials such as photocatalysts, catalysts, electrodes, and oxygen-carriers. In the most of cases, they are categorized into semiconductors based on their electronic energy structure: "band structure" composed of an electron-filled valence band (VB), electron-vacant conduction band (CB) and forbidden band (bandgap) separating CB and VB. However, it seems that the real band structure of metal oxides is still speculative and only conduction band bottom (CBB) and valence band top (VBT) positions have been discussed mainly, presumably because there have been no analytical methods to know the real band structures especially those at the surface. Another problem of characterization of metal oxides samples when they are mixed phase ones is a lack of a measure for how different kind of phases are contacted especially electronically though electronic contact between different kind of particles have been suggested to be decisive factor influencing the performance of materials.

A novel method, reversed double-beam photoacoustic spectroscopy (RDB-PAS), has been developed for identification and characterization of metal-oxide powders with energy-resolved distribution of electron traps (ERDT) measured. In RDB-PAS measurement, electrons in VB of metal-oxide samples are directly excited to electron traps (ETs) and accumulated in the ETs from the deeper side to the shallower side through wavelength-scanned continuous light. The electron-filled ETs caused the increasement of photoabsorption and the increasement can be detected by modulated light by PAS. In this study, ERDT analysis using RDB-PAS is expected to be applicable to estimation of band structure of metal-oxide samples and provides quantitative measurement of the interparticle electronic contacts. Chapter 1 describes those backgrounds and purposes of this study.

In Chapter 2, the candidate obtained experimental evidence of interparticle spatial overlapping of orbitals to result in interparticle charge-transfer excitation (ICTE), that is, photoexcitation from the higher DOS (density of states) part of the valence band (h-DOS(VB)) of the higher h-DOS(VB) sample to all ETs at an anatase-rutile interface proved by energy-resolved distribution of electron traps (ERDT) measured by reversed double-beam photoacoustic spectroscopy (RDB-PAS). The detailed energy-resolved distribution of electron traps (ERDT) analyses of various anatase-rutile mixtures revealed that all of the photoexcitation occurred from h-DOS in valence band of rutile in thoroughly mixed sample and h-DOS of rutile was located ca. 0.19 eV higher than that of anatase.

This is the first experimental results of practical h-DOS energy, which is related to practical photoabsorption of materials. Furthermore, the ICTE analysis suggested a new concept, mixing homogeneity, which can be quantitatively evaluated by comparison of ERDT patterns of mixture sample to simulated patterns with thoroughly adjoined mixture particles and non-contacted particles.

In Chapter 3, different kinds of titania mixtures were examined by ERDT analyses described in Chapter 2 and it was found that the maximum energy-shift ($\Delta E_{\max}$) values for most of the mixtures with rutile and anatase prepared by mix-H (thorough mixing by braying in an agate mortar for 10 min) were 0.18–0.19 eV. Due to the fact that the $\Delta E_{\max}$ obtained from the ERDT pattern with homogeneously mixed samples was constant with change in the anatase content, the constant $\Delta E_{\max}$ reflects the energy difference between h-DOS (VB)s of anatase and rutile in their mixture samples was ca. 0.20 eV. Anatase and rutile particles isolated from a typical commercial titania, Evonik P25, by a chemical dissolution method were characterized by RDB-PAS to estimate their band structure; the h-DOS(VB) of isolated-rutile (RUT) was same as those of most of commercial rutile samples. However, the isolated-anatase (ANA) showed an h-DOS(VB) position that was ca. 0.12 eV higher than most of commercial anatase titania samples presumably because the surface of anatase particles in P25 may be covered by a thin rutile layer to result in the ERDT pattern of ANA shifted to the low-energy side compared to the other anatase samples. Thus, RDB-PAS analysis of ERDT patterns of mixtures of different titania samples is expected to be a novel method to clarify the band-structure of semiconducting metal oxides such as titania.

In chapter 4, ERDT analysis of various anatase-rutile mixtures provided quantitative measurement of "mixing homogeneity" (how much proportion of one kind of particles (anatase in this study) are electronically contacted with the other kind of particles (rutile in this study)). This is a new concept and has not been measured so far, because such quantitative measurement requires macroscopic analysis collecting the information on particle contact; XRD and BET are representative macroscopic powder analyses, but they give no information on anatase-rutile particle contact, and SEM might give some information on anatase-rutile particle contact, but it is microscopic and no average can be obtained. The gas phase photocatalytic reaction performance of mixtures of anatase and rutile with different mixing homogeneity shown that good contact of anatase and rutile particles reduces the reaction efficiency. This suggests that the particle mixing-homogeneity degree may affects the photocatalytic activities.

In conclusion, the candidate obtained experimental evidence of interparticle spatial overlapping of orbitals to result in interparticle charge-transfer excitation (ICTE) at an anatase-rutile interface through ERDT measured by RDB-PAS. The detailed ERDT analyses of various anatase-rutile mixtures revealed that all of the photoexcitation occurred from h-DOS in valence band of rutile in thoroughly mixed sample and h-DOS of rutile was located ca. 0.2 eV higher than that of anatase. ERDT analysis using RDB-PAS is expected to be a novel method to clarify the relative band position of semiconducting metal oxides such as titania. In addition, the ERDT analysis suggested a novel concept, mixing degree which means "mixing homogeneity" in this study, could be quantitatively evaluated.