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Titania photocatalysis: New insights in the photocatalytic mechanism, and exemplary applications

(酸化チタン系光触媒反応：光触媒反応機構と典型的応用における新しい視点)

Although studies on titania photocatalysis were started more than a century ago and have been intensified during last four decades (after discovery of “Honda-Fujishima effect”), there are still many non-answered questions concerning the reason of high-low activity of titania photocatalysts and the clarification of key-factors of high activity. It is known that similar to catalytic reactions, small crystallite sizes and large specific surface area are responsible for high photocatalytic activity. However, in the case of photocatalysis, photoabsorption properties and intrinsic properties of distribution of electron traps are very crucial. Moreover, interactions between various phases in particular titania samples are also possible and could not be neglected. In this thesis, the most famous titania photocatalyst (P25) has been discussed. P25 exhibits one of the highest photocatalytic activities among titania samples, which could not be simply explained by its surface properties. A synergistic effect of co-existence of two crystal phases has been often reported as a reason of high photocatalytic activity, i.e., charge transfer between anatase and rutile resulting in retardation of charge carrier recombination. However, in those reports, there have been either no direct proof for such transfer or crystalline phases were not isolated from original P25. In contrast, a previous report from Ohtani laboratory showed that intrinsic activities of anatase and rutile were responsible for high activity of P25, but not anatase-rutile heterojunction, except methanol dehydrogenation with the highest activity for mixed-phase titania. In addition, various studies on P25 have not considered high nonuniformity of this sample (anatase content: 73-85%, rutile content: 14-17% and amorphous titania: 0-13%). Therefore, in this thesis, P25 sample was homogenized first, and all other experiments were performed for uniform P25 sample. It should be pointed that isolation methods by chemical dissolution, used for separation of crystalline phases, have also some shortcomings, i.e., the possibilities of formation of some impurities (from chemical reagents) on the surface of isolated phases. To avoid the influence of the impurities adsorbed on titania surface, post-treatment operations have been applied. Interestingly, it was found that rutile was more active than anatase and P25 for methanol dehydrogenation.

Therefore, it was confirmed that high activity of P25 was rather caused by intrinsic properties of anatase and rutile (high activities in various reactions) than interparticle charge transfer (IPCT) between anatase and rutile.

For hydrogen evolution, the presence of co-catalyst (platinum nanoparticles, Pt NPs) is necessary, and thus the amount and properties of Pt NPs should influence the overall photocatalytic activity. Therefore, in this thesis, the influence of Pt-loading amount on photocatalytic activity for methanol dehydrogenation has been investigated. It was found that maximum photocatalytic activity was obtained for much smaller content of platinum for isolated phases than that for P25, suggesting that post-treatment operations caused aggregation of titania particles, lowering the necessary amount of platinum deposits (one Pt deposit was sufficient on one particle/aggregate to enable photocatalytic reaction). Consequently, it was concluded that the interparticle electron transfer (IPET) between titania NPs inside one aggregate proceeded. This hypothesis was confirmed for P25 calcined sample at the same conditions as isolated phases resulting in lowering the necessary Pt-loading amount. This study is probably, the first confirmation of the IPET among the same particles (anatase $\rightarrow$ anatase or rutile $\rightarrow$ rutile), named here HOMO-IPET. Moreover, the action spectrum analyses indicated that rutile was platinized first, probably due to positively charged surface or IPET (anatase $\rightarrow$ rutile $\rightarrow$ Pt⁴⁺).

Moreover, the properties of Pt NPs have been examined in detail. It was found that slowing the photodeposition rate (by changing the initial conditions, e.g., from anaerobic to aerobic) resulted in preparation of non-aggregated Pt deposits, and such obtained photocatalysts exhibited higher photocatalytic activity. Moreover, this modified photodeposition method was successfully applied for other noble-metals, such as gold, silver and copper resulting in preparation of noble metal-modified titania samples possessing various properties, and thus different photocatalytic and antimicrobial properties. Exemplary applications of titania photocatalysts in the most urgent problems facing humanity, such as microbiological pollution and low quantum yield of photocatalysts under solar radiation, have been also investigated. Titania photocatalysts, prepared during this research, have been successfully applied for inactivation of microorganisms (bacteria and fungi) and decomposition of organic pollutants under visible light irradiation. For example, it was found that titania could be efficiently used as antifungal agent for various species of fungi. Another important finding is that even when mycelium growth was similar, the sporulation and mycotoxin generation was highly inhibited by light and titania presence.

The examination committee recognized that this thesis presents important findings, such as preparation of purified phases from mixed-phase titania, preferential platinization of rutile, and novel IPET between same kinds of nanoparticles (HOMO-IPET). The committee concluded that the applicant is eligible for the degree of Doctor of Philosophy (Environmental Science).