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Title	Titania photocatalysis : New insights in the photocatalytic mechanism and exemplary applications [an abstract of dissertation and a summary of dissertation review]
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Degree Grantor	北海道大学
Degree Name	博士(環境科学)
Dissertation Number	甲第13118号
Issue Date	2018-03-22
Doc URL	https://hdl.handle.net/2115/70401
Rights(URL)	https://creativecommons.org/licenses/by-nc-sa/4.0/
Type	doctoral thesis
File Information	Kunlei_WANG_abstract.pdf, 論文内容の要旨



学 位 論 文 内 容 の 要 旨

博士（環境科学）

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学 位 論 文 題 名

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 has started more than a century ago, and were 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 some 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. Therefore, one of the highest photocatalytic activities of titania P25 in various photocatalytic reactions which could not be simply explained by its surface properties, has been often reported as a reason of a synergistic effect of co-existence of two crystal phases: anatase and rutile. Many reports have been suggested a charge transfer between two phases, which should result in retardation of charge carrier recombination. However, in those reports, there have been either no direct proof for such transfer and crystalline phases were not isolated from original P25. A previous report from our laboratory confirmed that intrinsic activities of anatase and rutile were responsible for high activity of P25, but not anatase-rutile heterojunction, by using isolated phases of anatase and rutile. It should be pointed out that for hydrogen evolution (methanol dehydrogenation), the presence of co-catalyst (platinum nanoparticles, Pt NPs) is necessary, and thus the properties of Pt NPs should have influence on the overall photocatalytic activity. In addition, various studies on P25 did not consider high heterogeneity of this sample and the presence of amorphous phase. The previous report from our laboratory pointed out these two problems, clearly showing high heterogeneity of P25, i.e., anatase content: anatase 73-85%, rutile content: 14-17% and amorphous titania: 0-13%. In chapter 1, those backgrounds were described.

In chapter 2 of this thesis, in order to overcome the problem in previous report from our laboratory, homogenization of P25 sample was performed, and all other studies were performed for uniform P25 sample to avoid the influence of heterogeneity on data interpretation. Moreover, it should be also pointed out 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 operation has been applied. The photocatalytic activity tests for the reaction system of methanol dehydrogenation for isolated phases clearly showed that rutile phase was responsible for high photocatalytic activity of P25. Therefore, it could be concluded that high activity of P25 was not caused by anatase-rutile heterojunctions, but due to intrinsic high activity of rutile phase.

In chapter 3 of this thesis, first, the influence of Pt-loading amount on photocatalytic activity for methanol dehydrogenation was studied, resulting in maximum photocatalytic activity for much smaller content of platinum for isolated phases than that for P25, suggested 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). Therefore, 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 of necessary Pt-loading amount. This study is probably, the first confirmation of the IPET among the same particles (anatase or rutile), named here HOMO-IPET. Then, the action spectrum analyses indicated that rutile was platinized first, and its presence resulted in higher photocatalytic activity of rutile in the reaction of methanol dehydrogenation.

In chapter 4, as mentioned before, it was pointed out that the properties of platinum deposits are crucial for reaction of methanol dehydrogenation. Photodeposition method, is very convenient and fast, and results in preferential electronic-contact between titania and Pt since photogenerated electrons directly reduce platinum cations on the surface of titania. However, it should be pointed out that photodeposition is very fast in the case of platinum, and thus often aggregation of Pt deposits is observed, which could result in lowering of photocatalytic activities. It was found that slowing the photodeposition rate resulted in preparation of non-aggregated Pt deposits, and this method was also 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.

For the application of photocatalysis, the P25, homogenized P25 and isolated titania samples were tested for antifungal properties in the dark and under fluorescent irradiation. It was found that titania could be efficiently used as antifungal agent for various strains of fungi. In this thesis, the reason of high photocatalytic activity of titania was first explained by the HOMO-IPET, this is different from the general theory that the high photocatalytic activity of titania sample due to the co-presence of anatase and rutile. This kind of IPET is caused by the metal NPs deposited.