Chapter 2

PECULIARITIES OF THE REACTIONS ON PARTICULATE PHOTOCATALYSTS

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ABSTRACT

Some peculiar issues of photocatalytic reactions which may have been overlooked in many reports are reviewed. In the beginning, electron transfer (ET) initiated reactions at the solid surface, which is essential in photocatalysis, are classified to four types based on the extent of the interaction of the reactant with the solid surface. Those four ET reactions are reversible reactions, irreversible connected reactions, deposition, and dissolution. Most photocatalytic reactions are irreversible ET connected reactions and deposition of the products that strongly interact with the solid surface, while, in electrochemistry, reversible reaction for the reactants of weak interaction is mainly treated. Though the relationship between the reaction rate and the reaction energy has been discussed with the Marcus-Gerischer theory of electrochemistry, the acceptance of this

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theory for photocatalysis may cause difficulties because the frequency of the ET is limited by the photon absorption and the ET reaction rate is compete with the carrier recombination. Namely, the usage of the reorganization energy may need careful consideration for the kinetic analysis in semiconductor photocatalysis. The electric potential near the photocatalyst surface was visualized and it was realized that the potential gradient was localized near the surface holes, whereas it was expanded to the whole surface of the flat electrode in electrochemistry. Since the semiconductor photocatalysts are not wired to an electric source, the charges stored in the semiconductor particle can be evaluated. Then, a precise energy band position could be obtained and it may be different from the measurements by electrochemical methods, which was discussed in terms of the band alignments of anatase and rutile TiO_2 crystals. The analysis of the reaction kinetics for heterogeneous photocatalysis should be different from that for the homogeneous solution because a pair of the redox reactions take place in the same particle. Then, the novel method for applying the Langmuir-Hinshelwood equation was presented to describe the photocatalytic oxidation as a function of both the reactant concentration and the light intensity.

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