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Recent Studies on Heteropolyacid (HPA)/TiO₂ Hybrid Photocatalysts

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Abstract

Titanium dioxide (TiO₂) is an excellent photocatalyst for water and air purification. Because of the strong oxidation power of photogenerated holes from TiO₂, it can decompose almost all organic compounds. However, some limitations of its quantum yields remain because of its poor charge separation efficiency and its low Fermi level for O₂ reductions. Heteropolyacids (HPAs) are a subclass in a family of polyoxometalates (POMs), which are clusters of metal oxides that have a well-defined structure. Materials of this group enhance the photocatalytic activity of TiO₂ by a Z-scheme. Initially, the HPA(aq)/TiO₂(s) system was mainly studied. Recently however, transparent thin films of these hybrid materials have been prepared. Their unique properties such as excellent retention of the hydrophilicity after stopping UV illumination were reported. Herein, we review several recent studies that have examined these hybrid materials as photocatalysts.

Key-words: TiO2, Photocatalyst, Heteropolyacids

1. Introduction

Titanium dioxide (TiO_2) is a well known and important photocatalyst used for water and air purification¹). Because of the strong oxidation power of photogenerated holes from TiO₂, it decomposes almost all organic compounds under UV illumination. However, its quantum yield is not so high because of poor charge separation efficiency and its low Fermi level for O₂ reduction. Therefore, to date, various methods have been used to improve the photocatalytic performance of TiO₂, such as surface modification, morphology control, application of an external field, and a Zscheme design¹⁻¹⁰.

Additionally, the photoinduced hydrophilicity of a TiO_2 photocatalyst was discovered in 1995¹¹⁾. A highly hydrophilic surface is generated when UV is illuminated onto the TiO_2 surface. This surface exhibits both antifogging and self-cleaning properties. Polycrystalline TiO_2 film coatings have been applied to various industrial items¹²⁾. To date, two mechanisms have been proposed for this intriguing property: photocatalytic decomposition of surface organic contaminants¹³⁻¹⁵⁾ and photoinduced surface structural change^{16,17)}.

Heteropolyacids (HPAs) constitute a subclass in a family of polyoxometalates (POMs), which are clusters of metal oxides that have a well-defined structure¹⁸⁾. Actually, HPAs are metal oxide frameworks called polyanions that include heteroanions. They are acid catalysts because of their exceedingly strong Brønsted acid sites and are also photocatalysts by oxygen-to-metal and ligand-to-metal charge transfer ($O \rightarrow M$ LMCT) under UV illumination. Materials of this group

enhance the photocatalytic activity of TiO₂ by a Z-scheme¹⁹⁾. Initially, the systems of HPA(aq)/TiO₂(s) were mainly studied. Recently however, transparent thin films of these hybrid materials have been prepared. Their unique properties such as excellent retention of the hydrophilicity after stopping UV illumination have been reported²⁰⁾. This article presents a review of several recent studies that have examined this hybrid material system for use as a photocatalyst.

2. Heteropolyacids (HPAs)

2.1 POM structure

Polyoxometalates (POMs) are metal oxide clusters in a well-defined structure. Their chemical formula is based on $(MO_x)_n$; where M is usually Mo, W, or V. The POMs structure is divisible into three subsets¹⁸.

- (i) Heteropolyacids (HPAs) are metal oxide frameworks called polyanions that include heteroanions such as tetrahedra of PO₄³⁻ inside. Generally, they are represented by the formula of [X_xM_mO_p]ⁿ⁻, (M = W, Mo, V, Nb, Cr, and Ta and X = Si, P, etc.) consisting of an M-O octahedral basic structure unit. Keggin (XM₁₂O₄₀ⁿ⁻) and Dawson structures (X₂M₁₈O₆₂ⁿ⁻) are examples in this class. **Fig. 1**²¹) portrays these two structures.
- (ii) Isopolyanions are metal oxide frameworks without a heteroanion such as a Lindqvist structure $(M_6O_{19}^{n-})^{22}$.
- (iii) Molybdenum blue and molybdenum brown are reduced POM clusters. They contain molybdenum with high nuclearity in a pentagon building block unit such as the wheel-like (Mo₁₅₄O₄₆₂H₁₄(H₂O)₇₀)^{14–} and the ball-like Keplerate (Mo₁₃₂O₃₇₂(CH₃COO)₃₀(H₂O)₇₂)^{42–}.