

N=N bond cleavage of azobenzene through Pt/TiO₂ photocatalytic reduction

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TiO₂ photocatalytic 2e⁻-reduction of azobenzene to hydrazobenzene is found to occur at $\lambda_{\text{ex}} > 300$ nm while loading of nanometer-sized Pt particles on TiO₂ induces N=N bond cleavage via 4e⁻-reduction; only photoisomerization occurs in the absence of TiO₂.

From the viewpoint of "green chemistry", it is important to develop new processes for synthesizing useful compounds or detoxifying harmful compounds utilizing solar energy. Heterogeneous photocatalytic oxidations derived from valence band holes (h^+_{vb}) are attracting a great deal of attention for application to environmental problems.^{1,2} Much less interest has been shown in reductive photochemistry despite the fact that conduction band electrons (e^-_{cb}) have a potential to induce highly selective reduction because of their mild reducing power.³⁻⁶ Most of the azo dyes used widely in textile industries are carcinogenic and resistant to bacterial degradation, thus requiring effective wastewater treatment. The groups of Kiwi⁷ and Oliveira-Campos⁸ have recently reported photocatalytic oxidation of azo dyes using TiO₂ and Fe₂O₃. On the other hand, to our knowledge, the present work is the first study on heterogeneous photocatalytic reduction of azo dyes. Particular emphasis is placed on the loading effect of Pt nanoparticles on a TiO₂-photocatalyst.

Anatase TiO₂ particles (average diameter = 180 nm, BET surface area = 9.0 m² g⁻¹) were supplied from Tayca Co. (JA-1) and 0.1 wt% Pt was deposited on them by photodeposition (Pt/TiO₂).⁹ The particles (20 mg) were suspended in a 1.0 × 10⁻⁴ M solution [50 mL, solvent H₂O–EtOH (9/1 v/v)] of azobenzene (AB, > 95%, Tokyo Kasei Co.) in a double-jacketed cell. After the suspension had been purged with N₂ for 15 min, irradiation ($\lambda_{\text{ex}} > 300$ nm) was carried out with a 400 W high-pressure mercury arc (H-400P, Toshiba); the light intensity integrated from 320 to 400 nm ($I_{320-400}$) was measured as 3.4 mW cm⁻². N₂ bubbling and magnetic stirring of the suspension were continued throughout the irradiation while the reaction temperature was maintained at 31 ± 1 °C by circulating thermostatted water around the cell through the outer jacket. Product analysis was performed by both UV–VIS spectroscopy and high performance liquid chromatography [HPLC measurement conditions: column = Fluofix INW425 4.6 × 250 mm (NEOS); mobile phase H₂O–MeOH (1/1 v/v); flow rate = 3 mL min⁻¹; λ = 230 nm].

High-resolution transmission electron micrograph (HRTEM) images of Pt/TiO₂ demonstrated that Pt particles of diameter 2–5 nm are dispersed on the surface of TiO₂. The degree of adsorption of AB increased with loading of Pt (4.3 × 10⁻⁷ mol g⁻¹ for TiO₂ and 2.6 × 10⁻⁶ mol g⁻¹ for Pt/TiO₂ at an equilibrium concentration of 4.0 × 10⁻⁵ M), whereas the degree of adsorption of EtOH was essentially invariant with Pt loading. This finding indicates that AB and EtOH preferentially adsorb on Pt and TiO₂ surfaces of Pt/TiO₂, respectively. The interaction between AB and Pt would involve both σ -bonding [π orbital (AB) → d orbital (Pt)] and π -backbonding [d orbitals (Pt) → π^* orbital (AB)]. Aliphatic alcohols are known to adsorb strongly on the surface of TiO₂.¹⁰

The electronic absorption spectrum of AB showed two absorption bands at 423 and 321 nm assignable to the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions, respectively, for the *trans* isomer. The absorptivity of the $\pi \rightarrow \pi^*$ band for the *trans* isomer is 3.3 times that for the *cis* isomer.¹¹ The visible absorption at $\lambda > 400$ nm vanishes when the N=N bond of AB is broken. Accordingly, the $n \rightarrow \pi^*$ band is a good indication of the presence of the N=N bond. Without either TiO₂ (or Pt/TiO₂) or irradiation, the intensity of the $n \rightarrow \pi^*$ band was almost invariant, while that of the $\pi \rightarrow \pi^*$ band significantly decreased. This fact suggests that only *trans*–*cis* isomerization occurs under these conditions.¹² Also, Pt loading on TiO₂ increased the rate of isomerization in the dark. This is probably due to the decrease in the energy barrier for molecular rotation around the N=N bond with adsorption of AB on Pt surfaces. No products other than AB were detected from the irradiated solution by HPLC, which supports the above conclusion.

Fig. 1 shows the variation of the concentrations of AB and products in the presence of TiO₂ as a function of irradiation time (*t*). AB is slowly reduced to hydrazobenzene (HAB) with a selectivity of 97% at 0 < *t* < 3 h. Since the turnover frequency is calculated to be ca. 3 at *t* = 3 h, this reaction can be regarded as photocatalytic. In the absorption spectra, the $n \rightarrow \pi^*$ band gradually weakened concurrently with a rapid decrease in the $\pi \rightarrow \pi^*$ band intensity. Providing direct evidence for cleavage of the N=N bond.

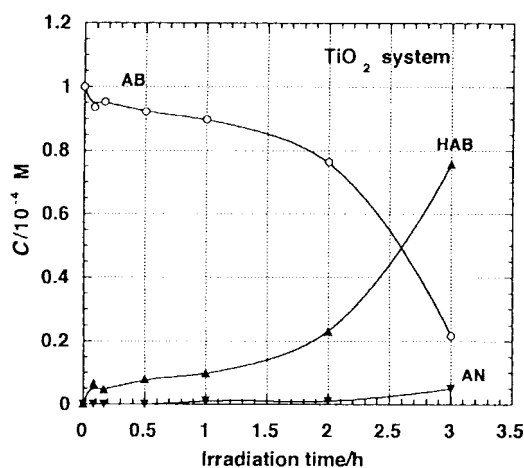


Fig. 1 TiO₂ photocatalytic reduction of AB at 31 ± 1 °C: initial pH = 6.4; TiO₂ 20 mg/50 mL.

Fig. 2 shows time profiles of the concentrations of AB and products with irradiation in the presence of Pt/TiO₂. The rate of reduction of AB to HAB markedly increases with loading of Pt [conversion ca. 100%, selectivity (HAB) = 91% at *t* = 1 h]. Noticeably, further reduction of HAB to aniline (AN) occurs [selectivity(AN) = 19.2% at *t* = 3 h]. In the absorption spectra, the $n \rightarrow \pi^*$ band of AB completely disappeared at *t* = 1 h and new absorption bands appeared at 280 and 230 nm at 3 h that are in accordance with the positions for the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$

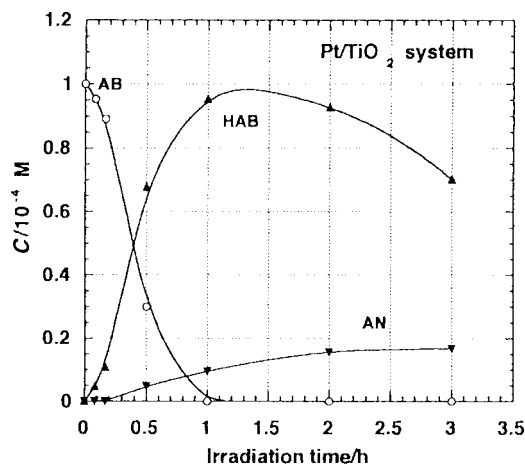


Fig. 2 Pt/TiO₂ photocatalytic reduction of AB at 31 ± 1 °C: initial pH = 6.5; Pt(0.10 wt%)/TiO₂.

bands, respectively, of AN. These facts are consistent with the results of Fig. 2. The pH of the Pt/TiO₂ system decreased from 6.5 ($t = 0$) to 5.6 ($t = 1$ h), while the corresponding change was very small for the unmodified TiO₂ system (Δ pH = 0.2). Product analysis by gas chromatography confirmed generation of MeCHO and CO₂ in each system. Evidently, EtOH acts as a reductant in the present photocatalytic reaction.¹³ It has been established that EtOH exerts a current doubling effect in TiO₂ photocatalysis,¹⁴ which would also be responsible for the reduction to proceed.

The results above clarified the two effects of Pt loading; one is to increase the rate of 2e⁻-reduction (AB→HAB) and the other is to enable 4e⁻-reduction (AB→AN). Pt loading enhances both the adsorption of AB (adsorption effect)⁴ and the charge separation of e⁻_{cb}...h⁺_{vb} pairs (charge separation effect).¹⁵ In addition, selective adsorption of the reactant (AB) on reduction sites (Pt) and the reductant (EtOH) on oxidation sites (TiO₂) is observed (reasonable delivery effect).¹⁶ The remarkable increase in the reduction rate can be explained in terms of these effects. Also, inspection of Fig. 1 and comparison with Fig. 2 suggests that Pt loading leads to the absence of an

induction period. Further the surface multi-electron transfer is thought to be assisted by an electron-pool effect of Pt with a large work function.

In conclusion, the 2e⁻-reduction of AB to HAB proceeds selectively by using TiO₂ as a photocatalyst, whereas only photoisomerization occurs in the absence of TiO₂. Loading of Pt on TiO₂ not only accelerates the reduction but also enables the 4e⁻-reduction of AB to AN. Our work thus represents a novel method for treating wastewater containing azo dyes via reductive cleavage of the N=N bonds.

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