PHOTOCATALYSIS ON TiO₂ IN ALKALINE SOLUTIONS

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Abstract

The investigation of the degradation process on TiO₂ films at high pH has to be done with consideration of a hydrogen-free surface, and the oxygen radical anion instead of the hydroxyl radical as possible reactant. A low redox potential of the pollutant oxidation compared to the energy of the valence band will favour the degradation of pollutant compared to the water oxidation. The redox potential of Cyanide oxidation is pH independent, contrary to the energy of the valence band, reaction conditions can be optimised by the variation of the pH.

Keywords: TiO₂, thin films, photocatalyst, cyanide-degradation, photoelectrocatalysis, solar light.

Introduction

The photocatalytic processes on TiO₂ are widely discussed for different pollutants in acidic solutions (e.g. Salvador 2011 [1]). The competition of direct photooxidation of water-dissolved pollutants with the indirect route via hydroxyl radicals in basic solutions (Fig. 1) is so far not discussed sufficiently.

![Fig. 1: Energy level model for an irradiated TiO₂/redox system (CN⁻/CNO⁻) in a pH 10 solution (anodic side under external bias)](image)

The need for high pH conditions is demonstrated with the treatment of cyanide. The production of highly volatile hydrogen cyanide is prevented in solutions of a pH higher than 9.2. For the comparison of the same species in different solutions from highly acidic to basic conditions, oxalic acid/oxalate is applied, which is characterised by its simple oxidation course.

Experimental

The TiO₂ film was synthesized, using a Titanyl Acetylacetonate in Methanol solution. The precursor was spray pyrolised (470°C) on FTO (spray pyrolysis)/soda lime glass.
Photoelectrochemical measurements were performed using a potentiostatic set-up with a bias of 1 V vs. Ag/AgCl. The catalyst coating on conducting glass (10 x 10 cm glass plates) served as working electrode vs. a polished stainless steel counter electrode and sat. Ag/AgCl as the reference electrode in a thin film reactor. The light source for the photoelectrocatalytic experiments was a fluorescent UVA lamp array (3 x 9 W).

Degradation of cyanide was done in a 0.01M NaOH solution. The degradation rate was followed with standard methods (AgNO₃/dimethylaminobenzalrodanine).

Results

The direct interfacial hole transfer mechanism for two model pollutants in alkaline solution is characterised by the following reactions:

\[ \text{CN}^- + h^+_x \rightleftharpoons \text{CN}^* \]  
\[ ((\text{COO})_2^-)_x + h^+_x \rightleftharpoons \text{COO}^{--} + \text{CO}_2 \]  

The competing reaction of the holes is the trapping of hydroxyl ions on the surface of the catalyst:

\[ \text{OH}^- + h^+_x \rightleftharpoons \text{OH}^* \]  

With density functional theory calculations of the surface structure of anatase and rutile, it can be shown that a variety of bonds is possible. Hydrogen atoms can be connected to surface titanium atoms in highly acidic solutions, hydrogen free surfaces can be found under basic conditions (Fig. 2).

Under these conditions, another radical reaction can be estimated:

\[ \text{O}^{2-} + h^+_x \rightleftharpoons \text{O}^{--} \]

an equilibrium with the hydroxyl radical is given by Neta et al. [3]

\[ \text{OH}^* + \text{OH}^- \rightleftharpoons \text{O}^{--} + \text{H}_2\text{O} \quad \text{pK} = 11.85 \]

The redox potential of this system will be independent of the process (indirect versus direct). By comparing the data of the literature with the results of the Cyanide degradation experiments, it can be shown that there is a relation between the difference of the redox potential of the pollutants to the energy of the valence band and the constant p (Fig. 3).

\[ p = \frac{kVF}{I_{	ext{photo}}} \]
p describes the ratio between the rate constant of the oxidation of the oxidisable additive (k) and the rate of water oxidation in a batch reactor with the total volume V of the solution, \(i_{\text{photo}}\) is the photocurrent produced with irradiation of UV-light. With this relation, a rate estimation based on thermodynamic parameters can be done.

As the oxidation of cyanide is pH independent (eq. 1), its redox potential will be close to the energy of the valence band at high pH.

![Graph](image)

**Fig. 3:** Linear free energy relationship – constant p against the difference of the energy of the valence band to the redox potential of different species [4]-[9].

**Conclusions**

On the surface of TiO\(_2\) the position of the atoms varies depending on the pH of the surrounding solution. The investigation of the adsorption of species on the TiO\(_2\) surface in alkaline solutions is an important factor for degradation experiments at high pH. Together with the analysis of the type of radicals, appearing under these conditions and their reactions, kinetic models for the degradation process of pollutants can be improved.

With the knowledge of the redox potential of the involved pollutant radicals, an estimation of the degradation rate can be done. A low redox potential of the pollutant oxidation compared to the energy of the valence band will favor the degradation of pollutant compared to the water oxidation. As the redox potential of Cyanide oxidation is pH independent, contrary to the energy of the valence band, reaction conditions can be optimised by the variation of the pH.

**References**


