Water Detoxification: Photocatalytic Decomposition of Phenol on Au/TiO₂

Anna Dobosz and Andrzej Sobczyński*
Faculty of Commodity Science, Poznań University of Economics, PL-60967 Poznań, Poland

Summary. Photodeposition of gold on TiO₂ was conducted in situ in the photoreactor used for the reaction of phenol photodestruction. The Au/TiO₂ system shows better photocatalytic properties in the destruction of phenol contaminants in water than pure TiO₂. The gold cocatalyst prevents also the decrease of the rate of the photocatalytic reaction at higher phenol concentration observed for pure TiO₂. Hydroquinone, p-benzoquinone, and catechol are main intermediates of the photoreaction, which finally leads to total phenol mineralization.

Keywords. Gold; Titania; Phenol; Photodegradation.

Introduction

Photocatalytic water purification on semiconductors is one of the newer AOP (Advanced Oxidation Processes) techniques, developed during the last two decades [1–9]. The process, which takes place on a surface of irradiated semiconductors, leads to water purification from organic substances. It is similar to those described earlier for semiconductor catalyzed hydrogen photogeneration from water in the presence of sacrificial agents [10–12]. In both cases, photogenerated holes react with hydroxyl groups from water giving hydroxyl radicals. The generated OH radicals react further with organic matter dissolved in water and cause its oxidation, finally to CO₂ and H₂O. Photogenerated electrons in deaerated water reduce H₃O⁺ causing hydrogen evolution. In aerated water, the electrons reduce dissolved oxygen.

Hydrogen evolution is not catalyzed well by the titaniaum dioxide surface. Therefore, it was necessary to modify the surface by introducing a cocatalyst improving H₃O⁺ reduction, recombination of the reduced hydrogen atoms to H₂, and gaseous product evolution. Besides platinum [13–17], also other cocatalysts like palladium [18], ruthenium [19], copper [20], nickel [21, 22], ruthenium dioxide [23], molybdenum, and tungsten sulfides [24, 25] have been applied. From the electrochemical point of view, islands of the noble metals or other substances on the TiO₂ surface act as microelectrodes (microcathodes) on which reduction processes occur [26].

* Corresponding author. E-mail: biuropromocji@novci1.poznan.pl
Besides, the bare titania surface catalyzes the reduction of oxygen dissolved in water. Therefore, photooxidation (mineralization) of organic water pollutants proceeds relatively efficiently on pure TiO$_2$ particles [1–9, 12]. However, it has been shown [27] that introduction of a Pt cocatalyst enhances the activity of titania in photoassisted oxidation of hydrocarbons dissolved in water. Based on theoretical considerations, Gerischer and Heller [28] suggested that the quantum efficiency of oxidation of organic compounds in water on illuminated $n$-TiO$_2$ was limited by the O$_2$ reduction rate. According to these authors, the semiconductor-like $n$-TiO$_2$ does not possess a sufficient density of shallow, near-surface electron traps to assist in the O$_2$ reduction process. It causes, in turn, accumulation of electrons on the semiconductor and acceleration of the rate of radiationless electron-hole recombination, a process which leads to a loss of the semiconductor photoactivity. To improve the efficiency of the photoreactions, they have suggested application of group VIII metals as cocatalysts. The authors’ predictions have been proven experimentally [29]. It has been found that incorporation of Pd$^0$ on titania particles promotes the electron transfer to O$_2$ dissolved in water, thus eliminating negative charge on TiO$_2$ and increasing the quantum efficiency of the photoassisted oxidation of 2,2-dichloropropionate. An increased rate of photodegradation of organic compounds like 1,4-dichlorobenzene and salicylic acid upon incorporation of Ag$^0$, Au$^0$, and Pd$^0$ onto the surface of TiO$_2$ particles has also been observed [30–32]. Recently, papers by Chen et al. [33–35] concerning the photocatalytic properties of Pt$^0$- and Pd$^0$-loaded titania particles have discussed kinetic processes and possible photocatalytic mechanisms which take place on the metallized surface of TiO$_2$.

In this paper, the photoactivity of Au/TiO$_2$ in phenol destruction is reported. The reagent was prepared by in situ metal photodeposition in the reaction slurry.

**Results and Discussion**

As mentioned above, metallic gold was photodeposited on the surface of TiO$_2$ in situ in the reaction vessel under a neutral atmosphere. For that purpose, the slurry of TiO$_2$ in an aqueous phenol solution to which an appropriate amount of HAuCl$_4$ 3H$_2$O had been previously added was purged with argon in order to remove dissolved oxygen. Next, the mixture was illuminated with a 180 W medium pressure Hg lamp for 30 min. It had been checked before that this illumination time was sufficient for the total reduction of metals like Pt [16], Ru [19], or Cu [20] on the surface of TiO$_2$. During the metal reduction the slurry was mixed by an argon stream applied at the bottom and flowing through a draft tube placed in the centre of the photoreactor. The photocatalytic reaction was conducted in a non-continuous mode (batch reactor).

The catalytic effect of Au on the photoactivity of TiO$_2$ has been studied previously by Gao et al. [30] in the reactions of 1,4-dichlorobenzene (DCB) and salicylic acid photodecomposition. The novelty of the present studies lies in the preparation of the Au/TiO$_2$ system. Here the metal was photodeposited on TiO$_2$ in situ, i.e. in the reaction environment. The method has been described previously for the preparation of such photocatalysts as Pt/TiO$_2$, Ru/TiO$_2$, and Cu/TiO$_2$ used in systems for hydrogen photogeneration from water in the presence of methanol as a sacrificial agent [16, 19, 20]. The method allows to omit steps like filtration/