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Photocatalytic oxidation of oxalic acid enhanced by silver deposition on a TiO_2 surface

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Abstract

Photooxidation of oxalic acid over TiO_2 surface in the presence of silver ion was studied. Simultaneous deposition of silver and oxidation of oxalic acid were followed under irradiation of aqueous suspensions of pH 2.5–3.5. The rate of the reduction of Ag^+ was increased by the progress of silver deposition until a considerable depletion of the silver ion in the liquid phase was achieved. Then it was slowed down when the transport of Ag^+ from the bulk of the liquid phase to the surface of the semiconductor particle became the rate-determining process. It has been demonstrated that, after the completion of silver deposition, the small metal particles on TiO_2 surface enhance the efficiency of the semiconductor by a factor of 5 for the photooxidation of oxalic acid.

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Keywords: Heterogeneous photocatalysis; TiO_2; Silver deposition; Oxidation; Oxalic acid

1. Introduction

Considerable attention has been devoted to study the photocatalytic degradation of organic and inorganic pollutants in order to reveal the mechanism of light initiated reactions and to apply them for solving environmental problems [1–4]. For this purpose TiO_2 is widely used as photocatalyst because its chemical stability and non-toxicity, electronic and optical properties [5–8]. Due to its relatively high band-gap energy, TiO_2 can utilize only a small fraction of the solar energy. Therefore, various methods have been employed to extend its absorption spectrum into the visible range. Molecular sensitizers such as transition metal complexes of ruthenium(II) bonded to the surface of the semiconductor particles have been proved to be efficient in solar cells converting the light to chemical energy [9–11]. However, for photomineralization of pollutants chemically more stable and especially cheaper modified TiO_2 is required [12–14]. Thus doping with simple transition metals is preferred. On the other hand, the presence of dissolved metallic ions is common in industrial waste waters as well in natural surface waters. It was found that metallic ions, principally Fe^{3+}, Cu^{2+} and Ag^+ increase the rate of photocatalytic oxidation of organic compounds, such as aromatic hydrocarbons, aromatic and aliphatic acids [15–18]. The reductive deposition of copper(II) ions photoassisted by TiO_2 in the presence of sacrificial electron donors (formate, oxalate) has been studied recently [19]. Sakata et al. [20] observed a large enhancement of the rate of photo-Kolbe reaction [21] of aliphatic acids with no hydrogen evolution in the presence of silver(I) ion. Influence of silver ions on the photocatalytic oxidation of *tert*-butanol over anatase was studied by Ohtani and co-workers [22–24]. Rutile, which is practically inactive in aqueous 2-propanol solution proved to be more efficient than anatase in the presence of Ag^+ [23]. These experiences indicated an efficient electron scavenging by Ag^+ instead of by H^+ that resulted in silver and the reduction in the efficiency of recombination of the hole–electron pair at the surface of the Pt/TiO_2. Oxygen evolution and silver deposition on the semiconductor particles were observed after illumination of TiO_2 powders suspended in aqueous Ag^+ solutions [25–27] and a molar ratio, n_{Ag}/n_{O_2}, close to the stoichiometric value of 4 was determined. Concerning the nature of the deposits Ohtani et al. [28,29] and Herrmann et al. [30] concluded that the Ag–O–Ti surface state was formed at the specific active sites of the surface where the Ag^+ had been adsorbed. The IR studies gave evidences of metallic silver formation in UV-irradiated paste prepared by TiO_2 and aqueous solution of $AgNO_3$ [31]. Formation of metallic silver spheroids of ca. 2 nm was pointed out by Herrmann et al. [30]. The type and the size of the particles of the deposited silver strongly depend on the type of TiO_2 [32]. A very poor dispersion of silver was detected by

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transmission electron microscopy (TEM) over rutile [33]. On the other hand, homogeneously distributed 2–8 nm particles were observed on the surface of P-25 particles, while larger, agglomerated particles of different shapes and size were found on BDH sample by TEM. The mechanism of silver deposit formation was studied using picosecond time resolved laser flash photolysis technique [34]. One electron, inner sphere reduction of Ag^+ by Ti^{III} was assigned as the rate determining step of the formation of the colloidal silver deposit, while the developing of nanosize silver aggregation was interpreted by two limiting mechanisms: (a) aggregation of concurrently formed silver atoms, and (b) a sequence of alternating electronic and ionic events [30] similarly to the latent image cluster formation in silver halide photography. Very recently a further progress in revealing the mechanism of the light-induced electron transfer reaction on the surface of transition-metal-loaded TiO_2 has been reported. Using femtosecond PP-DRS technique (PP-DRS—pump-and-probe diffuse reflectance spectroscopy), Ohtani and co-workers [35] pointed out that the recombination of $\{e^-, h^+\}$ pair is accelerated by transition metal (V, Cr, Fe, Co, Cu, Mo, W) loading at the surface of TiO_2.

In this contribution we discuss the results obtained by light-induced oxidation of oxalic acid over TiO_2 surface in the presence of silver ion. Our preliminary investigations indicated that the rate of photooxidation is influenced by various transition metal ions (e.g. Co^{2+}, Ni^{2+}, Cu^{2+}, Ag^+) and a considerable enhancement has been observed in the presence of Cu^{2+} and Ag^+. Addition of Cu^{2+} or Ag^+ to the suspension prepared by aqueous solution of oxalic acid and TiO_2 resulted in a typical conversion versus time curves under photolysis. These curves consist of two different sections. In the first section, where the reduction of the metal ions occurs, the rate of substrate oxidation is moderate and slightly increases especially in the presence of copper. The deposition of the metal on the TiO_2 is followed by the rapid photooxidation of the oxalate. So these systems offer the possibility for a careful study of the photoinduced metal deposition on the semiconductor surface and for investigation of the activity of the in situ metal loaded TiO_2. First, we paid more attention to the oxalic acid–silver–TiO_2 system because of the advantage of using a one-electron photoinduced redox process resulting in metal deposition. The other advantage of the studied system is that a simple analytical procedure is required to follow the reaction.

2. Experimental

2.1. Materials

The titanium dioxide (TiO_2) sample used in all experiments was Degussa P25, mainly anatase, with a surface area of ~50 $m^2 g^{-1}$. Silver solutions were prepared with Ag_2SO_4 (Reanal) of pure reagent grade. Oxalic acid and $KMnO_4$ were purchased from Reanal. The initial pH of the reaction mixture was adjusted using H_2SO_4 and NaOH of pure reagent grade. The other materials, such as NaCl were also reagent grade. The high purity water used in the experiments was double distilled and then purified with the Milli-Q system.

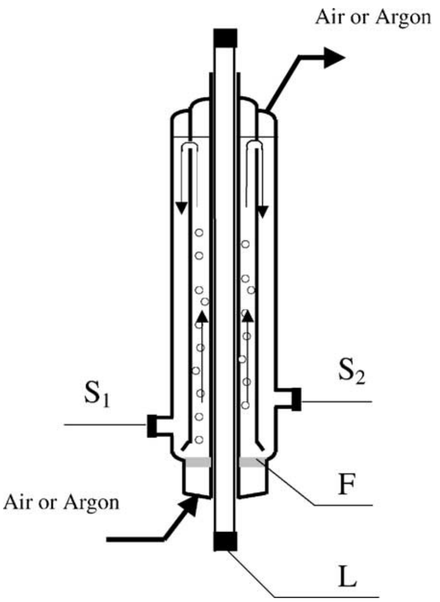

Fig. 1. Schematic representation of the photoreactor: L is the light source, S_1 a septum for feeding the photocatalyst, S_2 a septum for sampling and F a glass filter.

2.2. Photoreactor and photocatalytic experiments

The photochemical reactor developed for irradiation of the heterogeneous reaction mixture circulated by continuously fed air with a flow rate of 40 $dm^3 h^{-1}$ under irradiation is shown by Fig. 1. The light source (40 W, $\lambda_{max} = 350$ nm) is located at the central axis of the reactor having an internal mantle made by quartz. There is a glass tube between the internal (quartz) and external (glass) walls that separates the reactor of 3 dm^3 into two parts. The suspension of three phases (gas, liquid and solid) is moving up in the internal sphere and the reaction mixture consists of solid particles and solution is moving down in the external part. The gas (air or argon) leaves the reactor at the top and there is a septum for sampling near to the bottom of the reactor. The photon flux of the light source was determined by potassium tris(oxalato)ferrate(III) chemical actinometry. It was estimated to be 1.45×10^{-5} einstein s^{-1}. The initial volume of the photolysed reaction mixtures was 3 dm^3 in all experiments. The initial concentration of oxalic acid was 5×10^{-3} M and the initial concentration of silver sulfate was varied between 0 and 2×10^{-4} M. The concentration of TiO_2 was adjusted to 1 g dm^{-3} for heterogeneous systems.

2.3. Analyses

Before and after irradiation 4 cm^3 samples were taken through the septum with a syringe and immediately transferred to centrifuge tubings. The solid phase of sample ($4\,cm^3$) was separated by centrifugation at 6000 rpm for 10 min. The concentration of the oxalic acid was determined by classical permanganometry using the aliquot of the clear liquid sample. The concentration of silver ion was determined by potentiometric method using chloride ion selective electrode (CISE: Radelkis OP-271/1). The aliquot part of the clear aqueous solution of the sample was measured to another aliquot solution containing chloride ions and sodium nitrate in a given concentrations then it was completed with water to $5\,cm^3$ to obtain a sample of 0.3 M ionic strength and $T_{Cl} = 1.667 \times 10^{-4}$ M. Due to the reaction between the chloride and the silver ions silver chloride was formed resulting in a decreasing in the concentration of the free chloride ion. Its concentration was measured by CISE against the Ag/AgCl reference electrode. The concentration of the silver in the reaction mixture was determined considering the solubility product of the silver chloride and the mass balance of the silver as well as that of the chloride ions.

3. Results and discussion

Variation in the concentration of oxalic acid under irradiation of aqueous TiO_2 suspension at various initial concentration of silver is depicted in Fig. 2. When the oxalic acid is photolysed in the absence of silver ion the oxidation is relatively slow. The initial rate of the photochemical reaction is very similar in the presence of silver ion, however, it is rapidly increasing after a short period, which depends on the initial concentration of the silver ion (approximately 3 min for a solution of $[Ag^+] = 2 \times 10^{-4}$ M). The reaction rate is nearly constant in the second stage, which is about five times higher than that of measured in the absence of silver ion then it is leveling off when the concentration of the oxalic acid approximates to 0. It was found that in the first short period of the reaction the concentration of the silver ion in the liquid phase decreased rapidly and the color of the sample taken from the reactor through the septum as well as that of TiO_2 separated by the procedure described in Section 2 turned to pale brown. It is important to note that during this period a change in the color of the excited reaction mixture circulating in the reactor was also observed. The milky white suspension appeared to turn to bright green then this color deepened and finally its intensity seemed to be constant. First we have paid attention to study the silver deposition occurring under various conditions.

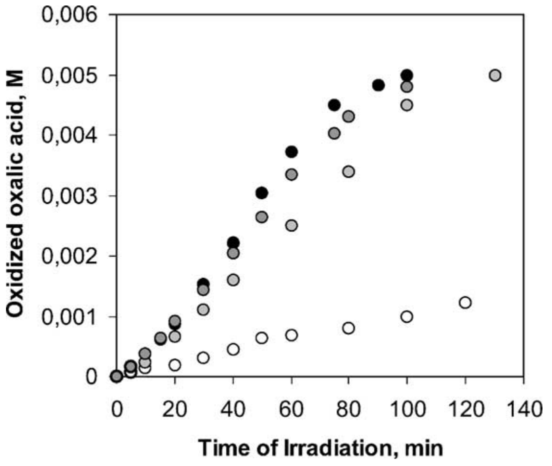

Fig. 2. Photooxidation of oxalic acid ($c_0 = 5 \times 10^{-3}$ M) at various initial concentrations of silver ion: (○) $[Ag^+]_0 = 0$, (◉) $[Ag^+]_0 = 3.5 \times 10^{-5}$ M, (◉) $[Ag^+]_0 = 1 \times 10^{-4}$ M, (●) $[Ag^+]_0 = 2 \times 10^{-4}$ M.

3.1. Silver deposition on TiO_2 surface

The reduction of silver was also investigated in a large-scale photochemical reactor. Fig. 3 shows the change in the concentration of Ag^+ under irradiation of various reaction mixture including homogeneous aqueous solutions as well as suspensions containing TiO_2. The figure clearly indicates enhanced photoreduction of silver ions in the presence of TiO_2. There are further remarkable features of the curves fitted to the data. Comparing the results obtained for both homogeneous solutions and heterogeneous reaction mixtures the rate of photoreaction is faster in the presence of oxalic acid than without this sacrificial electron donor. In addition, the rate of the reaction is increasing in suspensions until a relatively low silver concentration is achieved in the liquid phase. This apparent autocatalytic feature will be discussed later.

The photodeposition of the silver has been investigated using air and argon, respectively, for circulating the aqueous suspension. Fig. 4 demonstrates the decrease in the concentration of silver ion and the increase in the concentration of

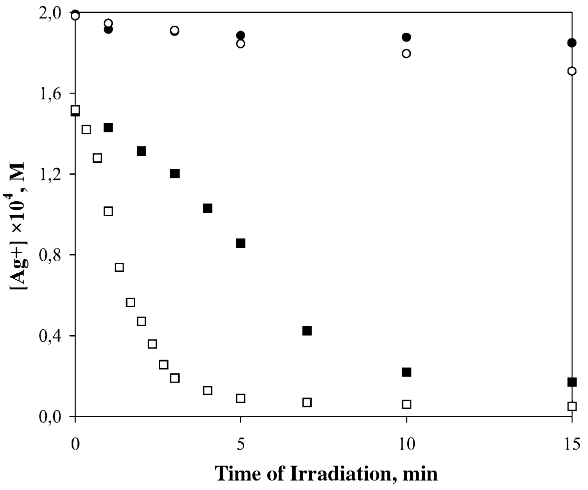

Fig. 3. Photoreduction of silver ion at various conditions: (●) in aqueous solution, (○) in aqueous solution in the presence of oxalic acid ($c_0 = 5 \times 10^{-3}$ M), (■) in the presence of TiO_2 ($1\,g\,dm^{-3}$), (□) in the presence of oxalic acid ($c_0 = 5 \times 10^{-3}$ M) and of TiO_2 ($1\,g\,dm^{-3}$). The initial analytical concentration of silver ion was 2×10^{-4} M in all experiments.

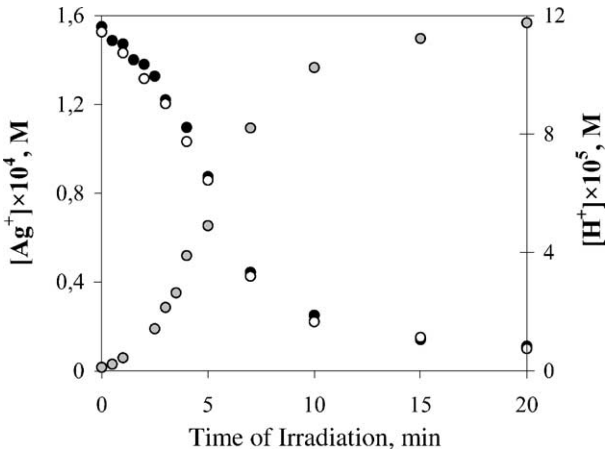

Fig. 4. Change in the concentration of silver ion (●, ○) and in the pH (◉) of the liquid phase under irradiation of the reaction mixtures of $c_{\mathrm{Ag}_0^+} = 2 \times 10^{-4}$ M and $c_{\mathrm{TiO}_2} = 1\,\mathrm{g\,dm^{-3}}$, using argon (●) and air (○).

the hydrogen ion in the aqueous phase. The data show that the rate of photoreduction of silver is not influenced by oxygen. It means that the electron scavenging by the oxygen at the surface of the excited semiconductor particle cannot efficiently compete with the electron transfer to the silver ion from the $\{e^-, h^+\}$ pair. So, the following reaction is a rather fast process comparing to electron transfer to oxygen molecule.

$$\mathrm{TiO_2}\{e^-, h^+\} + \mathrm{Ag}^+_{\mathrm{adsorbed}} \rightarrow \mathrm{TiO_2Ag^0}\{h^+\} \qquad (1)$$

The hole is trapped by the electron from the water molecule adsorbed on the surface of the semiconductor particle resulting H^+ and oxygen according to the stoichiometry given in Eq. (2).

$$4\mathrm{Ag}^+ + \mathrm{H_2O} \xrightarrow[\mathrm{TiO_2}]{h\nu} 4\mathrm{Ag}^0 + 4\mathrm{H}^+ + \mathrm{O_2} \qquad (2)$$

The rate of disappearance of silver ions from the solution and that of the formation of H^+ are continuously increasing up to a conversion of ca. 60%. These experiences suggest that the efficiency of the photoreaction (2) is increased by the small silver particles developing on the semiconductor surface. The silver deposition leads to the considerable change of the surface of the semiconductor resulting in a shift in its absorption spectrum to the visible range which is probably incident to the decreasing in the band-gap energy and provides an increase in the absorbed light fraction. Moreover, another effects of the silver deposition have to be also considered. Namely, due to the electronic interaction occurring at the contact region between metal deposits and the semiconductor surface the electrons are removed from TiO_2 into the vicinity of metal particle resulting in the formation of Schottky barriers [36]. This leads to an efficient charge separation of the light generated $\{e^-, h^+\}$ and therefore a more effective electron transfer to the electron acceptors adsorbed on the surface of the particle than in the case of the pure TiO_2.

The oxalate ion forms complex anion with Ag^+ ($\log \beta_{[\mathrm{Ag(C_2O_4)}]^-} = 3.65$) and acts as a sacrificial electron donor. Since the Ag^+ ions exist as aqua complexes in aqueous solution of Ag_2SO_4 and dominantly as $[\mathrm{Ag(C_2O_4)}]^-$ in the presence of oxalic acid of 10^{-3} M a higher rate for the adsorption of silver as well as a higher value for the surface complex formation are expected for oxalate system at pH ≈ 3, where the TiO_2 has positive charge (isoelectric point of the Degussa P25 is 6.6). In addition, it is also reasonable to suppose that in the presence of this sacrificial electron donor the rate of silver deposition is also increased. The size of the metallic silver deposition can increase rapidly by a sequence of alternating electronic event and ionic transport followed by adsorption, which results in metallic silver spheroids. Comparing the conversion and the rate of silver reduction under the photolysis of the aqueous suspension, both in the absence and presence of oxalic acid, a breakdown in the increase of the silver deposition rate is observed at various conversions (Fig. 5). This phenomenon can be interpreted by considering the silver ion transport to the surface followed by its adsorption. The adsorption of silver ions over the surface of TiO_2 particles is equilibrated within several minutes for the given concentration of the photocatalyst and that of the silver ion used in these experiments. Under irradiation when the photodeposition is very fast and the consumption of silver ions adsorbed on the surface is faster than its diffusion to the surface the rate of reduction is determined by diffusion of silver ions from the bulk to the surface. So the photoinduced electron transfer reaction is slowed down when the concentration of the silver ion is lowering in the aqueous phase. It is observed at 60 and ~40% conversion in the absence and presence of oxalic acid, respectively, which is expected by considering the enhancement of the reduction of silver ions in the presence of sacrificial electron donor. Upon silver deposition

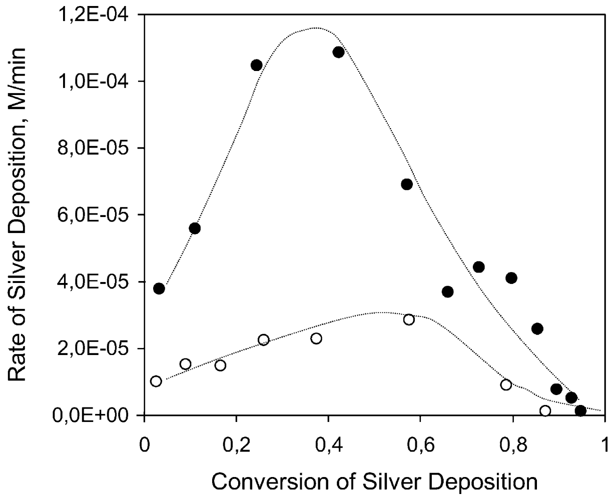

Fig. 5. Change in the rate of the silver reduction under the progress of silver deposition, in the reaction mixtures of $c_{\mathrm{Ag}_0^+} = 2 \times 10^{-4}$ M and $c_{\mathrm{TiO}_2} = 1\,\mathrm{g\,dm^{-3}}$: (○) $[\mathrm{H_2C_2O_4}]_0 = 0$ M, (●) $[\mathrm{H_2C_2O_4}]_0 = 5 \times 10^{-3}$ M.

oxalic acid is oxidized to CO_2. The change in the concentration of the silver ion and that of the oxalate was found to be equivalent according to the following equation:

$$2Ag^+ + H_2C_2O_4 + 2h\nu \rightarrow 2Ag^0 + 2CO_2 + 2H^+ \qquad (3)$$

3.2. *Photooxidation of oxalic acid over silver deposited TiO$_2$*

The rate of photooxidation of the oxalic acid is enhanced after the silver deposition has been completed (the concentration of the silver ion in the aqueous phase is lower than the limit of the analytical procedure) as it is demonstrated in Fig. 6. This figure clearly indicates that there is a change in the mechanism of the light-induced oxidation of the substrate. The silver deposits are act as electron traps. The photogenerated electrons are immobilized in these surface traps before being scavenged by electron acceptors adsorbed on the surface resulting in an improvement of the separation of electrons and holes. At this stage of the photoreaction it is the oxygen molecule that reacts as an electron acceptor. The electron transfer from the silver deposits to the oxygen should be a very fast process. However, it should be emphasize that it is slower than the electron transfer to Ag^+ ion. On the other hand, it is known that the reduction of oxygen is favorable in acidic media:

$$e^-_{Ag\ trapped} + O_{2\ ads} \rightarrow O_{2\ ads}{}^{\bullet -} \qquad (4)$$

$$O_2{}^{\bullet -} + H^+ \leftrightarrow HO_2{}^{\bullet} \qquad (5)$$

Because the electrons can be accumulated by the nanosize silver deposition, further electron can be readily transferred to the adsorbed $O_2{}^{\bullet -}$ as follows:

$$e^-_{Ag\ trapped} + O_2{}^{\bullet -} \rightarrow O_{2\ ads}{}^{2-} \qquad (6)$$

In principle there are several possible reactions for consuming the photogenerated holes that are trapped at or below the surface and identified as oxygen anion radical ($O^{\bullet -}$) covalently bound to titanium atoms.

(a) Oxalic acid acts as electron donor and the electron transfer resulted in $COOH^{\bullet}$ radical

$$h^+ + HC_2O_4{}^- \rightarrow CO_2 + COOH^{\bullet} \qquad (7)$$

The radical formed in this reaction can also react with dissolved oxygen to produce $HO_2{}^{\bullet}$

$$COOH^{\bullet} + O_2 \rightarrow CO_2 + HO_2{}^{\bullet} \qquad (8)$$

Because of the concentration of $COOH^{\bullet}$ should be lower than the concentration of oxygen molecule at the surface it is reasonable to exclude the recombination of $COOH^{\bullet}$ via bimolecular reaction with another $COOH^{\bullet}$ to oxalic acid.

(b) The adsorbed peroxide ion can dissociate to O^- which is able to transfer electron to the holes resulting in excited oxygen atom [37,38]. This very reactive species readily oxidizes the oxalic acid [39] as follows:

$$O_{2\ ads}{}^{2-} \rightarrow 2O_{ads}{}^- \qquad (9)$$

$$O_{ads}{}^- + h^+ \rightarrow O^* \qquad (10)$$

$$O^* + HC_2O_4{}^- \rightarrow O{=}C(OH)O^- + CO_2 \qquad (11)$$

$$O{=}C(OH)O^- + H^+ \rightarrow CO_2 + H_2O \qquad (12)$$

On the other hand one can exclude that the adsorbed water reacts efficiently with the holes to produce $OH^{\bullet}$ because the quantum yield for $OH^{\bullet}$ radical formation is much lower (7×10^{-5}) than that of holes (5.7×10^{-2}) according to the recent study of Hashimoto and co-workers

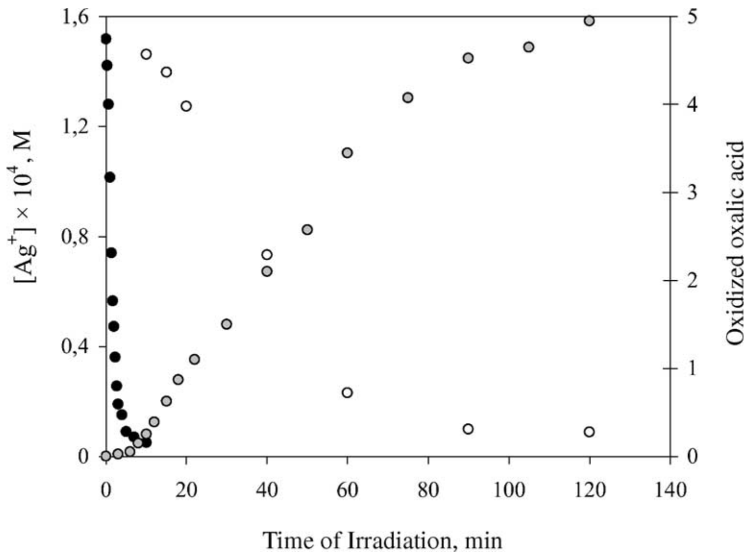

Fig. 6. Photooxidation of oxalic acid and photodeposition of silver under irradiation of the reaction mixture of $c_{Ag_0{}^+} = 2\times10^{-4}$ M and $c_{TiO_2} = 1\,g\,dm^{-3}$, $c_{oxalic\ acid} = 5\times10^{-3}$ M: (●) concentration of silver ion in the liquid phase, (◍) concentration of the oxalic acid, (○) pH.

[40]. However, hydroxyl radicals can be generated by the reactions of the peroxyl radicals:

$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \quad (13)$$

$$O_2^{\bullet -} + H_2O_2 \rightarrow OH^{\bullet} + OH^- + O_2 \quad (14)$$

$$H_2O_2 + h\nu \rightarrow 2OH^{\bullet} \quad (15)$$

$$H_2O_2 + e^-_{\text{Ag trapped}} \rightarrow OH^{\bullet} + OH^- \quad (16)$$

The hydroxyl radical readily oxidize the deprotonated form of oxalic acid with a rate coefficient of $4.7 \times 10^7\,M^{-1}\,s^{-1}$ [41]:

$$OH^{\bullet} + HC_2O_4^- \rightarrow COOH^{\bullet} + OH^- + CO_2 \quad (17)$$

Considering the above discussed electron transfer reactions as well as the reaction of various radicals it is concluded that the enhanced activity of silver modified TiO_2 can be attributed to: (1) the increase of the absorbed light fraction due to the shift in the absorption spectrum of the semiconductor to the longer wavelength; (2) the efficient separation of the light generated $\{h^+, e^-\}$ pair via trapping of electrons by the metallic silver deposited on the surface of TiO_2 resulting in an increase in lifetime this pair; (3) the increase in the probability of the formation of excited oxygen atom providing the following stoichiometry according to the reactions (4, 6, 9, 10, 11, 12):

$$2H_2C_2O_4 + O_2 + 2h\nu \rightarrow 4CO_2 + 2H_2O \quad (18)$$

This is in accordance with the model proposed by Hermann [39] for the photooxidation of oxalic acid over the excited TiO_2 surface. According to this model the excited atomic oxygen formed by the electron transfer from the O_{ads}^- to the hole is the dominant oxidizing agent for oxalic acid. It is important to emphasize that the molecular oxygen has two crucial roles in the oxidation of oxalic acid. First the oxygen molecules are very efficient electron acceptors especially at the silver deposited surface. Second, O_2 readily reacts with the $COOH^{\bullet}$ radical formed by the electron transfer from the $HC_2O_4^-$ to the photogenerated holes. In addition $O_{2\,ads}^{2-}$ formed by scavenging of two electrons consecutively or simultaneously by molecular oxygen adsorbed on silver deposited TiO_2 surface is the source of O_{ads}^-. So the formation of $O_{2\,ads}^{2-}$ is one of the most important processes resulting in the enhancement in the rate of photooxidation according to the pathway which is doubling the amount of oxidized oxalic acid (Eq. (18)) related to the reactions occurring under silver deposition (Eq. (3)).

4. Conclusions

Simultaneous silver deposition and photocatalytic oxidation of oxalic acid in excess was studied using TiO_2 at pH 2.5–3.5. The rate of photoreduction is increased by the progress of silver deposition until the transport of Ag^+ from the bulk of the liquid phase to the surface of the semiconductor particle becomes the rate-determining process. The presence of silver deposits on TiO_2 surface is found to enhance the efficiency of the semiconductor particle by a factor of 5 for the photooxidation of oxalic acid. The nanosize metallic silver particles on the TiO_2 surface can accumulate the electrons resulting in a better charge separation than in the case of bare TiO_2. This provides a more efficient electron transfer to the oxidizing and reducing molecules adsorbed on the surface of the particles than the recombination of holes and electrons. It has been also concluded that accumulation of the electrons in the nanosize silver particle increases the probability of the formation of excited oxygen atoms via electron transfer from the O_{ads}^- born from $O_{2\,ads}^{2-}$ to the hole.

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