

Study on photogeneration of hydrogen peroxide over ag/tio₂ catalysts in water

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Abstract

In the present study, catalytic photogeneration of hydrogen peroxide has been carried out in the presence of Ag-TiO₂ catalysts by using a batch reactor with a UV (36 watts) lamp. A series of Ag-TiO₂ catalysts (0.25-5%) was synthesized by the wet impregnation method and with a doping content of up to 5.0 wt% Ag at different calcination temperatures (200, 300, 400 and 500°C). The physic-chemical characteristics of the synthesized catalysts were characterized by powder X-ray diffraction (XRD), and Fourier transforms infrared spectroscopy (FT-IR). The photocatalytic activity of Ag-TiO₂ was evaluated in the H₂O₂ photogeneration in an aqueous solution in presence of formic acid under UV light illumination. The concentration of photogenerated H₂O₂ was estimated iodometrically. The results revealed that the yield of H_2O_2 photogeneration at optimum reaction conditions (176 ppm) was achieved.

Keywords: Photocatalysis; Titanium dioxide; H₂O₂ catalytic photogeneration; Superoxide; Hydroxyl radicals; UV irradiation.

Introduction

Hydrogen peroxide (H_2O_2) is one of the most important bulk chemicals in the world¹ that has widespread applications in many large-scale processes, including as bleaching and disinfecting². Such uses account for the majority of the H_2O_2 material manufactured. From a green chemistry perspective, hydrogen peroxide is the next most preferred oxidant, because water is the byproduct after oxygen donation³.

 H_2O_2 is produced around 2.2 million metric tons each year and demand for this chemical compound increasing 4 % per year⁴. At present, the

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dominating technology in producing H_2O_2 is anthraquinone auto oxidation (AO) process^{5,6} since, more than 90 % of all H_2O_2 is produced with this process^{1,7}. However, the AO process suffers from several drawbacks, such as use of complex and toxic solvent system, requirements of energy intensive process steps, high capital and operating costs that it is economically viable only for a large-scale production (>40 x 10³ tons per year), and additional safety concerns due to transportation of concentrated H_2O_2 solutions⁸. Nowadays the necessity of a simple production process which can be implemented at the point of use is the goal for the industries concerned⁹. Specially, practical applications of H_2O_2 only require dilute solutions¹⁰, in the range of 1-10 wt %¹¹. Therefore, onsite small scale processes for H_2O_2 production are of increasing interest because of the cost and hazards associated with the transport and handling of concentrated $H_2O_2^{12}$.

Although the direct synthesis of hydrogen peroxide from hydrogen and oxygen is in principle a more economic and environmental acceptable alternative to the classic anthraquinone route. To date it has found no industrial applications, despite a large number of patents filed over the past 30 years. This is due to two main basic reasons: (i) the need to avoid formation of explosive H_2/O_2 mixtures and (ii) the still unacceptable low selectivity of the reaction (whose main product is water)¹³.

Chemical syntheses using semiconductor photocatalysts can be environmentally benign processes that possess great potential for reducing energy consumption in industrial production of useful chemicals by using light energy¹⁴. The TiO₂ photocatalytic reactions are also interesting from the viewpoint of organic syntheses¹⁵. Photocatalytic generation of H₂O₂ from water is widely studied as a promising method for utilizing light energy to generate H₂O₂ as a useful chemical reagent¹⁶.

Photocatalytic reactions over semiconductor oxides have been investigated by Centi et. al¹⁷. Reactive O-containing species, namely OH, O₂, and H₂O₂, are usually formed at the surface of semiconductor oxides under UV irradiation¹⁸. Illumination of an aqueous suspension of TiO₂ particles at an energy above 3.23 eV (385 nm for anatase) excites an electron from the valence band (VB) to the conduction band (CB) of the semiconductor, while a positively charged holes is formed in the VB. The positive hole (h) oxides H₂O to form an OH radical, and the electron reduces O₂ to O[•] thus the edges of the VB and CB represent the oxidation and reduction sites, respectively, on a TiO₂ particle¹⁹.

Nanometric size titania is by far the most widely employed system in photocatalysis due to its comparatively higher photocatalytic activity, low toxicity, chemical stability, low cost²⁰⁻²² and commercial availability^{23,24}. In spite of the many benefits of TiO₂, a major limitation of achieving high photocatalytic efficiency is the quick charge carriers recombination which has faster kinetics than surface redox reactions and represents a major drawback as it reduces the quantum efficiency of the catalysis²⁵. To avoid this phenomenon, doping metal ions in the TiO₂ lattice has been used, such as silver²⁶. Ag is well known as good electron conductor which will help the electron transfer and therefore reduce the possibility of recombination of photogenerated electron-hole pairs²⁷.

Therefore, the aim of the present work was to investigate the efficiency of Ag-TiO₂ photocatalyst towards the photogeneration of hydrogen peroxide. In addition, the effect of different parameters in photogeneration of H_2O_2 such as catalyst load, initial formic acid concentration, catalyst dopant content, calcination temperature, and irradiation time were studied.

2. Experimental

2.1. Materials

Titanium dioxide (Merck, Darmstadt, Germany), silver nitrate (Panreac Quimca, SAU), and formic acid (90%, Lab. Chemicals, M&B Ltd., Dagenham, England). Reagents used for H₂O₂ determination were potassium iodide and potassium iodate (99.5%, Lab. Chemicals, M&B Ltd., Dagenham, England), ammonium molybdate (98%, Lab. Chemicals, Techno Pharmchem), sulphuric acid (98%, LOBA Chemie, India) and starch (Merck, Darmstadt, Germany). In all experiments, single distilled water was used except in catalyst preparation, double distilled water was used.

2.2. Synthesis of Ag/TiO₂ photocatalyst

Conventional wet impregnation method²⁸ was used for preparation of a series of Ag doped TiO₂ photocatalysts. Briefly, 5 g of TiO₂ were dispersed in a minimum amount of double distilled water with constant stirring. Calculated amounts of various loadings of AgNO₃ dissolved in bi-distilled water were added to TiO₂ suspension under stirring. The resulting slurry was stirred well for 1 h and allowed to settle, at room temperature overnight and then dried in an air oven at 105 °C for 24 h. The dried solids were ground in an agate mortar and calcined at different temperatures (200, 300, 400 and 500°C) for 5 h in a muffle furnace in static air. The contents of Ag were 0.25 - 5.0 wt %.

2.3.Characterization

X - ray diffraction (XRD) patterns of catalysts were obtained with the aid of Phillips diffractometer, type PW 2103, the patterns were run with Ni-filtered copper radiation (λ =1.5405) at 35 kV and 20 mA and scanning speed of 2° in 2ø min⁻¹.

Infrared analyses (IR) of the samples calcined at different temperatures were recorded in the 4000-400 cm⁻¹ regions with a Shimadazu spectrophotometer model (470), using the KBr disc technique. One mg of the substance as fine powder was mixed well with spectroscopically pure KBr

powder in an agate morter. The mixture was pressed in a special disc under vacuum of about 150 kg cm⁻² by means of a hydraulic press. The pure KBr disc produced was 1.2 cm diameter and about 0.7 mm thickness. The IR spectra were obtained for Ag-TiO₂ calcined at (300, 400, 500 °C) for 5 h in an air atmosphere.

2.4. Experimental design for photocatalytic process

The first set of experiments (Fig.1) concerning the optimization of reaction parameters were carried out in a 250 ml borosilicate glass beaker. In the second set , performed at optimized conditions, a pyrex cylinder (8 cm diameter, 25 cm height) of 600 ml total volume was used. A 36 watt medium pressure mercury lamp (Philips, Poland) of an emission wavelength of 365 nm, was used as the UV light source. In the first set of experiments, the lamp was positioned horizontally above the surface of the suspension at a fixed height (12 cm). In the second set, the lamp was mounted inside of glass sleeve with a diameter of (4.7 cm), positioned in the center of the reactor (Fig. 2). In all the experiments, the reaction mixtures in the reactor were maintained in suspension by magnetic stirring. Air was continuously bubbled in the second set of experiments, through a glass tube placed in the bottom of the reactor. While in the first one, the magnetic mixing guaranteed the oxygen required for the reaction from the atmospheric air. All experiments were carried out at $25 \pm 1^{\circ}$ C maintained in a controlled conditioned room.





Fig. (1): Experimental setup for first set of experiments.

Fig.(2): Experimental setup for second set of experiments.

2.5. Experimental procedure

Effect of various parameters such a catalyst concentration, stabilizer concentration, dopant ratio, irradiation time and calcination temperature were evaluated. 50 ml of suspension reaction were prepared by adding desired weight of the catalyst to the aqueous solution contains the required concentration of stabilizer. Prior to photoreaction, the suspension was magnetically stirred in a dark condition for 30 min to establish an adsorption/desorption equilibrium status then irradiated under UV-A light for 2 hr. After that, the analytical sample was taken from the suspension with the help of 10 ml plastic syringe and immediately filtered through a 0.45 μ m Millipore filter to remove the catalyst particles. The filtrate was analyzed for determining the concentration of H₂O₂. At optimized conditions, 200 ml of suspension reaction was prepared and irradiated for 4 h under the conditions of second set of experiments.

2.6. Determination of H₂O₂ concentration

 H_2O_2 concentration was determined by the modified iodometric method²⁹. The procedure, was as follows: to 50 ml of the solution containing H_2O_2 , 0.5 ml of concentrated sulphuric acid (d 1.84), 0.2 ml of a normal ammonium molybdate solution, and 0.3 g of potassium iodide were added. The solution, after being kept in the dark for about 10 minutes, was titrated against N/ 100 sodium thiosulphate solution, using a standardized burette, after the addition of 2 ml of freshly prepared starch solution.

3. Results and discussion3.1. Ag/TiO₂ characterization3.1.1. XRD results

XRD patterns of undoped and Ag-TiO₂ with different Ag content are shown in Fig. 3. All the observed diffraction peaks were indexed by anatase TiO₂ in agreement with JCPDS card No. 12-1272³⁰. Moreover, no additional peaks belonging to Ag species are observed, suggesting that the Ag metal most probably exists in the form of mono-dots (nano-clusters) that are well dispersed on TiO_2 surfaces³¹, and therefore cannot be detected with X-ray diffractometer because of the Ag small amount. This may indicate also that the metal dopants are merely placed on the crystals surface without being covalently anchored into the crystal lattice. Hence, these metal sites are expected to be below the visibility limit of X-ray analysis^{31,32}. The effect of calcination temperature on the catalyst containing 3 wt % Ag on the X-ray patterns was carried out and the results are shown in Fig. 4. It shows that upon increasing calcination temperature from 200 up to 500 °C, all dopant samples exhibit a crystalline structure. In addition no new peaks were observed rather than those corresponding to TiO₂. Moreover, the intensity of the main peak at $2\Theta = 25.3$ increases on increasing the dopant from 3 to 5 wt % Ag.



Fig. 3 :X-ray diffraction for Ag/TiO₂ at different Ag doses, calcinated at 300 °C for 5 h.



Fig. 4: X-ray diffraction for 3% Ag/TiO₂ calcinated at different temperatures for 5 h.3.1.2. FT-IR results

FT-IR spectra of pure and Ag doped TiO₂ were studied and presented in Figs (5,6). Fig. 5, pure TiO₂ exhibits a broad band centered at ≈ 3500 cm⁻¹ which is attributed to OH stretching and a small broad band at 1650 cm⁻¹ due to the OH bending mode of water adsorbed on the surface of TiO₂ which may have critical roles in photocatalytic activity³³. Because they can interact with

photogenerated holes, which gives better charge transfer and inhibits the recombination of electron-hole pairs³⁴. The broad band at \approx 400-760 cm⁻¹ was attributed to Ti-O stretching and Ti-O-Ti bridging stretching mode³⁵. The addition of Ag into TiO₂ led to increase the intensity of the peak located at 1650 cm⁻¹. This means that increase the number of surface OH groups. Fig. 6 shows that the effect of calcination temperature of 3 wt % Ag on the intensity of main groups of the surface of TiO₂. It can be seen that, upon increasing calcination temperature from 300-500 a remarkable decrease in the intensity of peak was assigned at \approx 1650 cm⁻¹. This is due to the decrease of the surface hydroxyl groups.



Fig. 5: Infrared spectra for Ag/TiO₂ at different Ag doses, calcinated at 300°C for 5 h.



Fig.6: Infrared spectra for 3% Ag/TiO₂ calcinated at different temperature for 5 h.

3.2. Effect of operating parameters

Regarding the comparable conditions requirement, atmospheric oxygen needed in the first set experimental conditions was guaranteed by magnetic stirrer.

3.2.1. Effect of catalyst load

In order to examine the effect of Ag-TiO₂ catalysts dose on the photogeneration of H₂O₂, experiments were set up with varying amount of catalyst dose (from 0.1 to .6 g) while keeping initial formic acid concentration of 0.05 M and irradiation time at 2 h. The results are illustrated in Fig.7. It could be seen from Fig. 7 that the concentration of H₂O₂ seems to increase with increasing catalyst weight from 0.1 to 0.4 g after that no significant increase was observed. This behavior may be attributed to the increase in the number of active sites available on the catalyst surface³⁶ which accompanying with the increase number of hydroxyl and superoxide radicals³⁷. Further increase in the catalyst weight (0.6 g) causes the photocatalytic reaction to decrease. This decrease may be explained as: (i) the light screening effect of TiO₂ particles, which reduces the penetration of light

in the photoreactor and also the amount of active sites being photonactivated³⁸. (ii) agglomeration and sedimentation of photocatalyst particles are also possible^{36,39}, which, a part of the catalyst surface probably become unavailable for photon absorption thus bringing little stimulation to the catalytic reaction³⁶, and (iii) deactivation of activated molecules by collision with ground state molecules:

$TiO_2^* + TiO_2 \rightarrow TiO_2^{\#} + TiO_2$

where TiO_2^* is the TiO₂ with active species adsorbed on its surface and TiO₂[#] is the deactivated form of TiO₂⁴⁰.



Fig. 7: Effect of catalyst weight on the yield of H₂O₂.

3.2.2. Effect of Ag content

To evaluate the effect of dopant % on the H_2O_2 yield and find out the optimum content of Ag impurity, a set of experiments with an initial concentration of Ag-TiO₂ of 200 mg L⁻¹ under UV-A irradiation was carried out in aqueous suspension using Ag-TiO₂ catalysts with a Ag content between 0.25 and 5.0 wt. %. The experimental results are shown in Fig. 8. It shows that, as Ag content increases, H_2O_2 concentration increases up to 3%

Ag. It implies that the Ag dopant promotes the charge pair separation efficiency for TiO₂ catalyst⁴¹. The enhanced activity of TiO₂ by doping with Ag may be attributed to the electronic interaction occurring at the contact region between the metal deposits and the semiconductor surface. This may cause the transfer of the electrons from TiO₂ into the vicinity of the metal particle resulting in the formation of Schottky barrier leading to charge separation⁴². Such transfer is thermodynamically possible because the Fermi level of TiO₂ is higher than that of Ag metal⁴³. The Ag deposits acting as electron traps⁴⁴ immobilization the photogenerated electrons in the traps shortly transferring them to oxygen to form highly oxidative species such as $^{\circ}O_{2}^{-45}$. This type of electron scavenging by Ag is reported to be faster process compared to the electron transfer to oxygen (or) recombination with holes⁴⁶. Since, the traping of electrons by Ag from TiO₂ occurs at a faster rate when compared to the electron transfer from TiO_2 to O_2^{47} enhanced photogeneration of H₂O₂ has been observed since the recombination of electron - hole pair has prevented. On the other hand when Ag load exceeds the optimum value, the excess amount will be detrimental towards the photocatalytic activity of the catalyst. This may be attributed to:

(i) Excessive coverage of TiO₂ catalyst limits the amount of light reaching to the TiO₂ surface, reducing the number of photogenerated e^- - h^+ pairs and lowering consequently the TiO₂ photoactivity²⁴. In addition, metal deposits may occupy the active sites on the TiO₂ surface for the desired photocatalytic reactions causing the TiO₂ lose its activity⁴⁸.

(ii) Negatively charged silver sites begin to attract holes and subsequently recombine them with electrons. In this case, the metal deposits become recombination centers²⁴.

(iii) The probability of the hole capture is increased by the large number of silver particles at high silver loadings, which decrease the probability of holes reacting with adsorbed species at the TiO_2 surface⁴⁹.



Fig. 8: Effect of dopant concentration on the yield of H₂O₂.

3.2.3. Effect of formic acid dosage

Hole-scavengers are chemical species added into a photocatalytic system in order to stabilize the photogenerated holes. This is carried out in order to prevent the electron-hole recombination process. They are usually easily oxidized organic compounds⁵⁰. It has reported using formaldehyde, acetaldehyde, formic acid, acetic acid, methanol, ethanol, 2-propanol, butanol and azo dye as hole scavengers^{51,52}. The effect of formic acid concentration on the generated amount of H_2O_2 was carried out and the results are presented in Fig. 9. It shows that upon increasing the formic acid concentration of 0.2 M. Further increase, no significant change in H_2O_2 yield is observed. This may be explained on the basis that, on increasing the formic acid concentration, the photogeneration rate of H_2O_2 increases as more formic acid concentration, the photogeneration rate of H_2O_2 increases as more formic acid concentration, the photogeneration rate of H_2O_2 increases as more formic acid molecules are available for hole scavenging (i. e., charge separation). Also, with an increase in formic acid concentration beyond 0.2 M, the

solution becomes more dense and the path length of photons entering the solution is decreased thereby fewer photons reached the catalyst surface. Hence, the production of hydroxyl and superoxide radicals participating in the H_2O_2 photogeneration are reduced and consequently the photogeneration efficiency is reduced.



Fig. 9: Effect of formic acid dose on the yield of H_2O_2 .

3.2.4. Effect of calcination temperature

The photocatalytic activity of TiO₂ mainly depends on its crystalline nature, phase composition, surface area and particle size⁵³ in addition to the ratio between anatase and rutile phases⁵⁴ as well. Heat treatment of catalyst samples could alter the catalyst structure, particle size, as well as photoactive phase of TiO₂ crystalline⁵⁵. Calcination will inevitably cause a decrease in area, surface loss of surface hydroxyl groups and even phase transformation⁵⁶. The effect of calcination temperature on the catalytic activity performance of TiO_2 doped with 3 wt. % Ag on the generation concentration of H₂O₂ was studied on the catalysts calcinated from 200 to 500 °C under the reaction conditions and the results are shown in Fig. 10. The results show that the H_2O_2 yield decreases with increasing calcination temperature up to 500 °C.

In conclusion from the results depicted in Fig. 10 that, the increase in calcination temperature leads to a decrease in H_2O_2 yield, due to a decrease of surface hydroxyl groups as predicted from FTIR results.



Fig. 10: Effect of calcination temperature on the yield of H_2O_2 .

3.2.5. Effect of irradiation time

The effect of irradiation time on the photogeneration of H_2O_2 under reaction condition was studied employing three different values namely 2, 4, 6 h and the results are shown in Fig. 11. It demonstrates that H_2O_2 yield increases with increasing irradiation time up to 6 h, as more charge carriers are generated with time.



Fig. 11: Effect of irradiation time on the yield of H₂O₂.

3.2.6. Mechanism of H₂O₂ formation

Hydrogen peroxide can be formed either by reduction of oxygen to form super-oxide radicals O_2^{\bullet} (Reaction 1) which are in equilibrium with hydro-peroxide radicals in presence of protons (Reaction 2).

$$O_2 + e^- \rightarrow (O_2^{-})s$$
 (1)

$$(O_2^{\bullet})s + H^+ \rightarrow (HO_2)s$$
 (2)

These radicals can be further reduced by electrons (Reaction3) and then form hydrogen peroxide (H_2O_2) (Reaction 4).

$$(\mathrm{HO}_{2}^{\bullet})\mathrm{s} + \mathrm{e}^{-} \rightarrow (\mathrm{HO}_{2}^{-})\mathrm{s}$$
(3)

$$(\mathrm{HO}_{2}^{-})\mathrm{s} + \mathrm{H}^{+} \rightarrow (\mathrm{H}_{2}\mathrm{O}_{2})\mathrm{s}$$

$$\tag{4}$$



Fig. 12: Possible reaction pathways of the photocatalytic generation of H_2O_2 from water and oxygen⁵⁷.

Another potential route for formation of hydrogen peroxide is the oxidation of water by photo - generated holes, forming hydroxyl radicals (Reaction5), which can dimerize at the surface of the photocatalyst (Reaction 6)⁵⁸.

$$H_2O + h^+ \rightarrow OH^{\bullet} + H^+$$
(5)

$$\mathbf{OH}^{\bullet} + \mathbf{OH}^{\bullet} \to \mathbf{H}_2\mathbf{O}_2 \tag{6}$$

3.3. Results at optimum reaction conditions

According to results obtained in the first set of experiments, optimum conditions were established which are: catalyst load of 0.4 gL⁻¹, silver catalyst content of 3 %, catalyst calcination temperature of 200 °C, formic acid concentration of 0.2 M, , and irradiation time of 4 h. Moreover, due to the vital role of oxygen in the photocatalytic process as an electron acceptor facilitating carrier charge separation, oxygen (i. e atmospheric oxygen) was bubbled in the reaction medium which enable more efficient mixing of the catalyst as well. Furthermore, the UV lamp was mounted inside of glass sleeve. In such optimum conditions, photogenerated H₂O₂ yield was raised up to 176 ppm.

Conclusion

In the present work, pure and silver-doped TiO_2 catalysts were synthesized through wet impregnation method. An enhancement of the photocatalytic activity of TiO_2 catalyst by doping with silver has been confirmed in the photogeneration of H_2O_2 . It was found that with a suitable amount (3 wt%), the Ag dopant effectively increases the photocatalytic activity of the TiO₂. Silver deposits on the TiO₂ surface behave as sites where electrons accumulate. Better separation of electrons and holes on the modified TiO₂ surface, allows more efficient channeling of the charge carriers into useful reduction and oxidation reactions rather than recombination reactions. The results presented in this paper indicate that Ag/TiO₂ photocatalyst could be used to photogenerate H₂O₂. The maximum yield of H₂O₂ (176 ppm) was obtained upon irradiation of an aqueous solution containing 0.4 g/l of 3 % Ag-TiO₂ in presence of formic acid under UV light illumination for 4 h.

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تم فى هذا البحث دراسة تكوين فوق أكسيد الهيدروجين ضوئياً باستخدام أكسيد التيتانيوم

المدعم بأكسيد الفضة كعوامل حفازة وذلك على نطاق معملى باستخدام مفاعل صمم لهذا الغرض

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مزود بلمبة أشعة فوق بنفسجية (36 وات). حيث تم تطعيم العامل الحفاز بتركيزات مختلفة (25. - 5 ٪) من عنصر الفضة بطريقة التشرب ثم تحميص العينات المحضرة عند درجات حرارة مختلفة (200-500°م). أجرى توصيف الحوافز الاولية والمحمصة باستخدام حيود الاشعة السينية والاشعة تحت الحمراء. تم تقييم الكفاءة الضوئية للعامل الحفاز من خلال تتبع تركيز فوق أكسيد الهيدروجين الناتج فى وجود حمض الفورميك بعد تعرضه للأشعة فوق البنفسجية. وقد اكدت النتائج امكانية الحصول على 176 جزء / مليون من فوق اكسيد الهيدروجين بعد تشعيع المعلق لمدة 4 ساعات.

