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Hydrogen peroxide and photocatalysis

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ABSTRACT

The formation, the adsorption and the degradation of H_2O_2 on different commercial TiO_2 samples (anatase, rutile) and on ZnO have been investigated to better understand its participation in the photocatalytic reactions.

The Langmuir and Langmuir–Hinshelwood models have been used for determining the adsorption constants and the rate constants of H_2O_2 disappearance on these different photocatalysts both in the dark and under UV-A irradiation.

Interaction between H_2O_2 and TiO_2 has been investigated by UV–vis spectroscopy.

The adsorption of H_2O_2 on TiO_2 samples is discussed in term of surface area and nature of TiO_2 including the number of OH groups present on the photocatalysts. The nature of the yellow complex formed between H_2O_2 and TiO_2 is discussed taking into account its stability, and the coverage rate of OH groups.

The kinetic of H_2O_2 disappearance on the different photocatalysts is related to the adsorption but also the energy of conduction band of anatase and rutile photocatalysts.

The results of the formation and decomposition of H_2O_2 under UV-A irradiation in the presence of ZnO photocatalyst are explained in light of its adsorption.

1. Introduction

TiO_2-based photocatalysis is considered as an efficient process to remove air or water pollutants and it is well established that O_2 is essential in the process. It is also well known that electrons and holes generated react with H_2O and O_2 to form Reactive Oxygen Species (ROS) such as $OH^{\bullet}$, $HO_2^{\bullet}$, $O_2^{\bullet-}$, H_2O_2. Among the various Reactive Oxygen Species present in the mechanism of photocatalysis, H_2O_2 is the most stable species. H_2O_2 can serve as a reservoir of active ROS. Actually, some papers show the formation of $O_2^{\bullet-}$, $HO_2^{\bullet}$ or $OH^{\bullet}$ depending of conditions and nature of catalyst [1–3] and one of our previous publication has also shown the participation of H_2O_2 in the photocatalytic degradation of organics [4].

H_2O_2 is a very simple molecule but its behavior on semiconductor is very complex. Actually, it can be formed but also decomposed during the photocatalytic process.

It can be formed either by reduction of oxygen to form superoxide radicals $O_2^{\bullet-}$ (Reaction (R1)) which are in equilibrium with hydro-peroxide radicals in presence of protons (Reaction (R2)) [5].

$$O_2 + e^- \rightarrow (O_2^{\bullet-})s \tag{R1}$$

$$(O_2^{\bullet-})s + H^+ \rightarrow (HO_2^{\bullet})s \tag{R2}$$

These radicals can be further reduced by electrons (Reaction (R3)) and then form hydrogen peroxide (H_2O_2) (Reaction (R4)) [5].

$$(HO_2^{\bullet})s + e^- \rightarrow (HO_2^-)s \tag{R3}$$

$$(HO_2^-)s + H^+ \rightarrow (H_2O_2)s \tag{R4}$$

Another potential route for formation of hydrogen peroxide is the oxidation of water by photo- generated holes, forming hydroxyl radicals (Reaction (R5)), which can dimerize at the surface of the photocatalyst (Reaction (R6)) [3]. Considering, the adsorption energy of the HO radicals onto the surface of TiO_2 ($\Delta E = -4\,eV$) [6], this most likely makes their desorption and recombination a process with a positive ΔG at room temperature.

$$H_2O + h+ \rightarrow OH^{\bullet} + H^+ \tag{R5}$$

$$OH^{\bullet} + OH^{\bullet} \rightarrow H_2O_2 \tag{R6}$$

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However, it is very difficult to observe and quantify H_2O_2 due to its rapid decomposition on TiO_2 catalysts either by reduction (Reaction (R7)) or oxidation (Reaction (R8)) [5–9]. However some publications mentioned H_2O_2 in the gas phase near TiO_2 surfaces [10]. Nosaka et al. succeeded in quantifying the amount of H_2O_2 during photocatalysis. They found a H_2O_2 concentration in the order of the nmol/L [11].

$$H_2O_2 + 2e^- + 2H^+ \rightarrow 2H_2O \tag{R7}$$

$$H_2O_2 + 2h^+ \rightarrow O_2 + 2\,H^+ \tag{R8}$$

Taking into account that H_2O_2 can serve as a reservoir of more active ROS and that the impact of these relatively stable ROS on the mechanism of photocatalysis is not clear, in this work we propose to investigate the impact of the surface area and of the nature of TiO_2 (anatase, and rutile) on the adsorption and the decomposition of H_2O_2 but also on the UV–vis absorption properties. The formation and decomposition of hydrogen peroxide on ZnO is also studied because of its similar band gap and the absence of adsorption of H_2O_2 on this semiconductor. A relation between adsorption, nature and disappearance rate will be discussed.

2. Experimental

2.1. Photocatalysts and H_2O_2

One commercial Zinc oxide from Sigma–Aldrich and seven commercial titanium dioxide were used: titania Degussa P-25 which is made of anatase (80%) and rutile (20%), a 100% rutile sample from ISK (Ishihara Sangyo Kaisha), Japan; five anatase structures: PC105 and PC500 titanium dioxide from Millennium, AN1 and AN2 from Nanostructured and Amorphous Materials Inc and Hombikat UV100 purchased from Sachtleben Chemie (Duisburg, Germany). The characterizations of these catalysts, given by the producer of these commercial catalysts, are introduced in Table 1. H_2O_2 at 50% in water from Sigma–Aldrich is used in our experiments.

2.2. Photoreactor and light source

Irradiation was performed in a 1 L cylindrical glass reactor. Irradiation was provided by a 125 W UV-lamp Philips HPK placed in a plunging tube. A Pyrex cylindrical jacket located around the plunging tube contained circulating water to absorb IR radiation and avoid heating of the solution. The irradiance is measured by a digital radiometer (VLX-3W, UVItec) and was of 4 mW/cm^2.

2.3. Experimental procedures

2.3.1. Adsorption

A volume of 750 mL of aqueous solution with various initial concentrations of H_2O_2 was stirred in the dark in presence of photocatalyst at a concentration equal to 0.5 g L^{-1}. Ultrapure water (18 MΩ cm^{-1}) from Millipore Waters Milli-Q purification unit was used for all experiments. The concentration of the catalyst (0.5 g/L) has been chosen for a full absorption of the incident photon flux. Samples were withdrawn at regular intervals, centrifuged and analysed in order to monitor the H_2O_2 concentration.

2.3.2. Photocatalytic procedure

Before irradiation, H_2O_2/photocatalysts mixtures were stirred in the dark until the adsorption equilibrium was reached. Then, samples were collected from the reactor at regular time intervals and filtered through 0.45 μm millipores Durapore discs to remove photocatalyst powder before analysis.

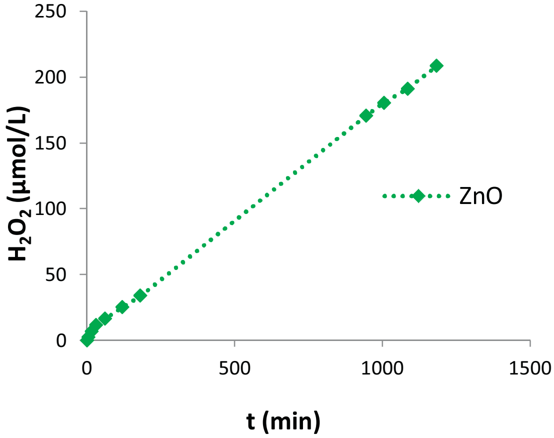

Fig. 1. Formation of H_2O_2 as a function of irradiation time in presence of 0.5 g/L of ZnO and water.

2.3.3. Analysis

H_2O_2 was complexed with an acidic solution of $TiCl_4$. Then, the H_2O_2 content of each sample was monitored at 410 nm by performing UV–vis spectroscopy in order to detect the yellow complex formed under acidic conditions in the presence of Ti^{4+} ions [12,13].

The UV–vis absorption spectra of complex formed between photocatalyst and H_2O_2 were recorded using a CCD Spectrometer Avantes AvaSpec-ULS2048. An optical fiber cable with a cosine corrector (CC-UV/VIS) enables punctual light emission measurements. The cosine corrector diameter is 3.9 mm for a measurement area of 12 mm^2.

3. Results and discussion

3.1. Formation of H_2O_2 on TiO_2 and on ZnO photocatalysts

Before studying the decomposition of H_2O_2 on illuminated various TiO_2 and on ZnO, we investigated the production of hydrogen peroxide and evaluated the impact of the surface area. H_2O_2 was detected only in the case of TiO_2 having a surface area higher than 200 m^2/g. However, the amounts are very low and correspond to less than 0.02 μmol/L. So, it seems that high surface areas favor the production of H_2O_2. Unfortunately, taking into account the very low concentration of H_2O_2 detected, these results do not allow us to clearly conclude on the impact of the surface and structure of TiO_2. In the presence of ZnO, a continuous formation of H_2O_2 was observed with a rate of about 0.18 μmol/L/min (Fig. 1).

The low concentration of H_2O_2 detected in presence of illuminated TiO_2 aqueous suspension, is in agreement with the literature [14,15]. For example, Nosaka et al. [11] reported the detection of H_2O_2 in concentrations as small as 10^{-9} M in presence of TiO_2. Boonstra et al. [16] suggested that the different behaviors of TiO_2 and ZnO can be explained by the absence of adsorption of H_2O_2 on zinc oxide. Our results given in Section 3.2.1 are in agreement with this hypothesis showing the necessity of interaction between photocatalyst surface and H_2O_2 to be degraded.

To better understand the pathways of production of hydrogen peroxide, hole scavengers have been used by different authors [5,17–19]. All these works reported that the presence of scavengers of holes on TiO_2 anatase improved the formation of H_2O_2. Moreover, Tafalla et al. [20] showed that an increasing in oxygen in the suspension improves the production of H_2O_2. These different works, performed on anatase TiO_2 samples, are in agreement with the production of H_2O_2 mainly by reduction of oxygen.