

## Selective Oxidation Processes of Organic Substances by Means of Photocatalytic Systems

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Selective oxidation of benzyl alcohol to benzaldehyde in aqueous solution, at acidic conditions, through TiO<sub>2</sub>/Cu(II)/solar UV system was investigated. Different commercial TiO<sub>2</sub> samples were tested. The best result found in terms of yield was of 35 % of benzaldehyde with respect to the initial benzyl alcohol. During each run a partial conversion of benzaldehyde to benzoic acid was also observed. The study suggested that different operative parameters, such as the composition of photocatalyst, amount of catalyst, pH, ionic components in water and the initial concentration of Cu(II) played an important role in the photocatalytic oxidation of benzyl alcohol. At the end of the process, Cu(II) could be regenerated and reused, through a re-oxidation of Cu(0), produced during the photolytic run, with air at dark.

### 1. Introduction

Titanium oxide photocatalysis is one of the most studied process to oxidize organics by means of a solar UV source and oxygen (or air) (Kabra et al., 2004; Chong *et al.*, 2010). The mechanism of reaction that makes possible the process has been extensively investigated and includes the photochemical formation of an electron-hole pair on TiO<sub>2</sub> as the key step which starts the process itself (Herrmann, 2005). Titanium oxide photocatalysts have a great potential also as a versatile tool in "green" organic synthesis. Several photocatalytic transformations hold significant promise for the development of economically and environmentally friendly synthesis processes (Palmisano et al., 2010). It is also well known that the substitution of oxygen with a species capable of reducing by trapping the electrons in the conducting band still enables the oxidation of the organic species. Of particular interest is the case in which oxygen as reducing species is replaced by a metal ion in the solution. The latter reduces to a lower oxidation state by capturing the photogenerated electrons on TiO<sub>2</sub> whereas the organic species oxidizes through a direct reaction with the positive holes (h<sup>+</sup>) or with OH radicals. In some cases, the reduction of the metal results into its precipitation from the solution thus enabling its separation and recovery. The reduction of many metals such as Cu(II), Ni(II), Pb(II) and Zn(II) has been investigated in the past (Kabra et al., 2007). Among the others, some papers have been devoted to the photoreduction of Cu(II) ions in the presence of simple organic species such as organic acids (Canterino et al., 2008), alcohols (Foster et al., 1995) in the absence of oxygen. It has been reported that the simple admission of air into the system, at the end of the process, allows the re-oxidation of precipitated copper which completely dissolves. The overall behaviour of the system can be described in the two stages: in the first, the reduction of copper allows the oxidation of the organic compound, in the second air reoxidizes Cu(0). It is evident

that the role of copper (in the presence of TiO<sub>2</sub> and UV) is that of a photocatalytic species (moving between two (or three) different oxidation states, (0 and or +1 and +2), which makes possible the oxidation of the organic substances by air at ambient conditions. On basis of this consideration, the use of Cu(II)/TiO<sub>2</sub>/UV as a photocatalytic system to oxidize organic species by air can be proposed. Benzaldehyde is the simplest and industrially the most important aromatic aldehyde. Benzaldehyde is used in a large number of applications, among the others, as an industrial solvent and commercial food flavouring. Benzaldehyde is produced principally by the hydrolysis of benzal chloride or the partial oxidation of toluene (Ullmann's 2005). Both these processes employ very hard operating conditions and cause wastewater disposal problems. In the present work the possibility to use the system Cu(II)/TiO<sub>2</sub>/UV for the selective oxidation of benzyl alcohol to benzaldehyde is studied at varying the operating conditions (TiO<sub>2</sub> type, catalyst load, copper ions concentration and pH).

## 2. Experimental

Experiments were carried out in a batch cylindrical glass reactor (280 ml) equipped with high-pressure UV lamp (Helios Italquartz), thermostated at 298 K. The pH was regulated with phosphoric acid. In all the experiments the solution was preventively purged with helium. During the runs a gaseous stream of helium was continuously fed to the irradiated magnetically stirred solution to prevent the dissolution of atmospheric oxygen. The concentrations of benzyl alcohol, benzaldehyde, benzoic acid and cupric ions at different reaction times were evaluated by HPLC analysis. BET specific surface areas were measured by the single-point BET.

Four commercial microcrystalline TiO<sub>2</sub> powders were studied: (1) TiO<sub>2</sub> Degussa P25 (80% anatase, 20% rutile, BET area 50 m<sup>2</sup> g<sup>-1</sup>), (2) TiO<sub>2</sub> Aldrich (pure anatase phase, BET area 9.5 m<sup>2</sup> g<sup>-1</sup>), (3) TiO<sub>2</sub> Aldrich (pure rutile phase, BET area 2.5 m<sup>2</sup> g<sup>-1</sup>), TiO<sub>2</sub> Aldrich (rutile phase with small amount of anatase, BET area 2.7 m<sup>2</sup> g<sup>-1</sup>). Copper sulphate, benzyl alcohol, Benzaldehyde, benzoic acid, phosphoric acid, were purchased from Sigma Aldrich.

## 3. Results and Discussion

Preliminary runs in the presence of the substrate and Cu(II) ions, without TiO<sub>2</sub> or with TiO<sub>2</sub> and without Cu(II) addition to the solution, did not result into any conversion of benzyl alcohol even for long reaction times. Moreover benzyl alcohol did not show any tendency to undergo direct photolysis.

In fig 1 the results obtained during a run of photooxidation of benzyl alcohol with different TiO<sub>2</sub> commercial samples are shown. The diagrams show that the reactivity of benzyl alcohol is strongly influenced by the type of TiO<sub>2</sub> used in the experiment. In particular, the best results in terms of conversion are observed when Aldrich TiO<sub>2</sub> (pure anatase) was used in the run. In this case, after 120 minutes of reaction, the concentration of Cu(II) approached zero with a conversion of the alcohol of about 75 %. Last data invariably indicate the existence of parasitic reactions in which other species consume the positive holes thus reducing the consumption ratio, alcohol/Cu(II), to a value lower than 1.0.

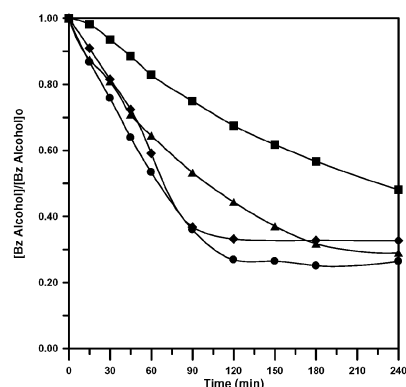


Figure 1: Photooxydation of Benzyl Alcohol - Effect of  $\text{TiO}_2$  type.  $[\text{Cu(II)}]_0 = 1.50 \text{ mM}$ .  $[\text{TiO}_2]_0 = 200 \text{ mg/l}$   $[\text{Benzyl Alcohol}]_0 = 1.50 \text{ mM}$ . • Aldrich (pure anatase), ◆ P25, ▲ Aldrich (pure rutile), ■ Aldrich (prevalently rutile).

Moreover, during the process the substrate is mainly converted into benzaldehyde which only partially further oxidizes to benzoic acid (fig.2). When the highest conversion of benzyl alcohol was achieved, 35 % of it resulted to be converted into benzaldehyde and only 8 % into benzoic acid for pure anatase  $\text{TiO}_2$ .

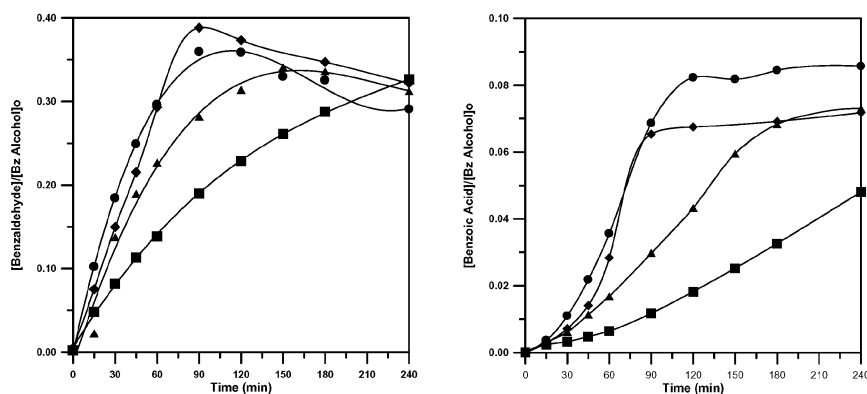


Figure 2: Effect of  $\text{TiO}_2$  type: Benzaldehyde (left) and benzoic acid (right) production.  $[\text{Benzyl alcohol}]_0 = 1.50 \text{ mM}$ .  $[\text{Cu(II)}]_0 = 1.50 \text{ mM}$ .  $[\text{TiO}_2]_0 = 200 \text{ mg/l}$ : • Aldrich (pure anatase), ◆ P25, ▲ Aldrich (pure rutile), ■ Aldrich (prevalently rutile)

The decrease of  $\text{Cu(II)}$  concentration was accompanied by the precipitation of a purple solid. At the end of a single run, the solid was filtered, washed, newly suspended in a volume of distilled water- equal to that used for the run -and poured again into the reactor. An air stream was then fed to the reactor and- after about 60 minutes- the  $\text{Cu(II)}$  concentration reached approximately the same value as that at the beginning of the run . The system thus obtained was used for a new oxidation run after dissolving the substrate and submitting it to UV irradiation (data not shown). The results obtained with the same  $\text{TiO}_2$  but at different  $\text{Cu(II)}$  concentrations are reported in fig. 3.

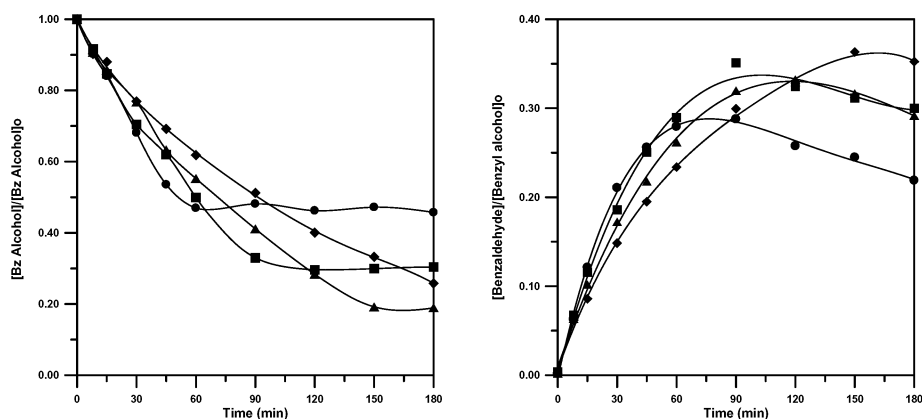
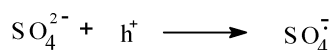


Figure 3: Effect of initial Cu(II) concentration: Benzyl alcohol consumption (left) and benzaldehyde production (right).  $\text{TiO}_2$  (Aldrich, pure anatase) = 200 mg/l.  $[\text{Benzyl alcohol}]_0 = 1.50 \text{ mM}$ .  $[\text{Cu(II)}]_0$ : • 1.12 mM, ■ 1.42 mM, ▲ 1.84 mM, ◆ 2.30 mM.

A higher initial concentration of Cu(II) resulted into a decrease of the reactivity as can be verified by comparing the half-life time for the substrate which passed from 55 to 120 min. respectively for  $[\text{Cu(II)}]_0$  equal to 1.12 mM and 2.30 mM. Since the salt used to prepare the solutions is cupric sulphate, it is evident that any increase of Cu(II) resulted into one of sulphates that can react with the positive holes formed:



The effect of  $\text{TiO}_2$  load was successively investigated by carrying out some oxidation experiments in which different amounts of the photocatalyst per liter were added to the reacting solutions (fig. 4).

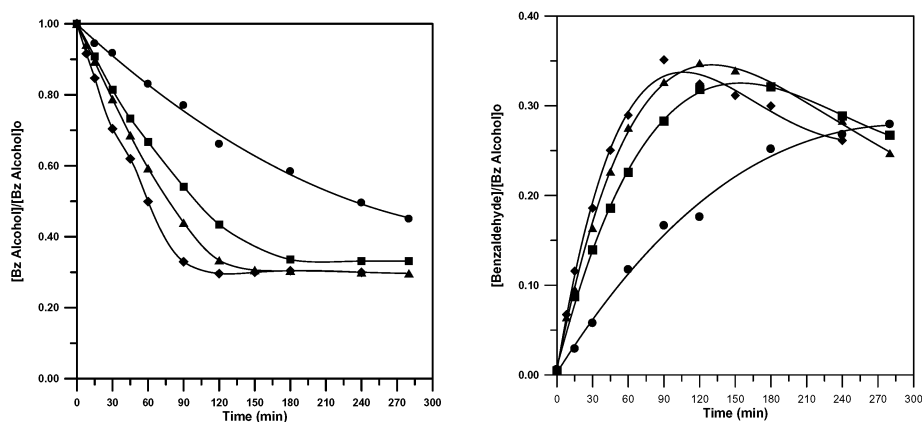


Figure 4: Effect of  $\text{TiO}_2$  load. Benzyl alcohol consumption (left) and benzaldehyde production (right).  $[\text{Benzyl alcohol}]_0 = 1.50 \text{ mM}$ .  $[\text{Cu(II)}]_0 = 1.50 \text{ mM}$ .  $\text{TiO}_2$  (Aldrich, pure anatase): • 55 mg/l, ■ 100 mg/l, ▲ 150 mg/l, ◆ 200 mg/l.

An increase of the catalyst load resulted into a marked increase of the system reactivity with the half-life time for the substrate. An increase of  $\text{TiO}_2$  load, for values higher than 200 mg/l, did not result into an increase of system reactivity probably due to a significant scattering of radiation.

The results obtained at varying the pH, in the range 2.0 - 4.0, are shown in fig. 5:

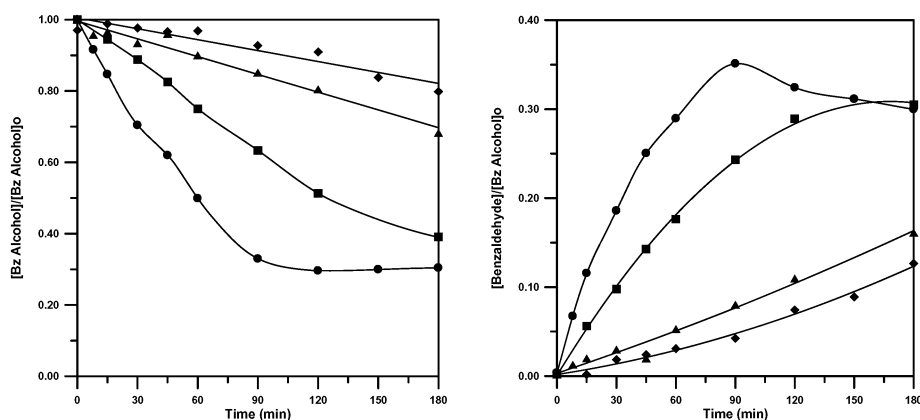


Figure 5: Effect of pH. Benzyl alcohol consumption (left) and benzaldehyde production (right).  $[\text{Benzyl alcohol}]_0 = 1.50 \text{ mM}$ .  $[\text{Cu(II)}]_0 = 1.50 \text{ mM}$ .  $\text{TiO}_2$  (Aldrich, pure anatase) = 200 mg/l. ● pH = 2.0, ■ pH = 2.5 ▲ pH = 3.0, ◆ pH = 4.0.

A decrease of benzyl alcohol consumption and benzaldehyde formation rate by increasing the pH was observed. It can be supposed, according to the  $\text{pH}_{\text{zpc}}$  equal to 4.2 for the adopted  $\text{TiO}_2$  Aldrich sample (Jungho Ryu and WonYong Choi, 2008), that an increase of the pH from 2.0 to 4.0 reduces the concentration of positive charges on the catalyst surface partially inhibiting the adsorption (and the reactivity) of the substrate. On the other hand, since  $\text{H}_3\text{PO}_4$  was used to adjust the pH of the reacting solutions, being known the capability of  $\text{H}_2\text{PO}_4^-$  ions to react with the positive holes formed on the catalyst after irradiation (Chun Hu *et al.*, 2004), for any increase of pH resulting into a higher concentration of these ions, a strong inhibition of the direct oxidation of the substrate may be expected.

#### 4. Conclusions

The possibility to oxidize benzyl alcohol to benzaldehyde in aqueous solution, at acidic conditions, using the photocatalytic system  $\text{TiO}_2/\text{Cu(II)}/\text{solar UV}$  has been studied in the present work. Four samples of  $\text{TiO}_2$  characterized by different crystallographic forms and specific surface areas have been used during the experiments. The best result found was a yield of 35 % of benzaldehyde with respect of the initial benzyl alcohol. Benzaldehyde has been also partially converted to benzoic acid. At the end of the process copper (II) was totally reduced to copper (0), which could easily be reoxidized to Cu(II), at dark, in the presence of oxygen.

The effect of the catalyst load, the nature of the inorganic anions ( $\text{H}_2\text{PO}_4^-$ ), the initial Cu(II) concentration and pH of the solution has been also investigated. The di-

hydrogen-phosphate anion resulted to exert a negative effect on the photooxidation rates of benzyl alcohol and to behave as scavengers towards surface HO radicals. A decrease of benzyl alcohol oxidation and benzaldehyde formation rates has been observed by increasing the pH from 2.0 to 4.0.

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