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## **Production and recovery of acetaldehyde through selective photo-oxidation of ethanol over Cu/TiO<sub>2</sub> nanocatalyst in aqueous solution**

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### **1. Introduction**

The continuous exhaustion of fossil-material-derived fuels and the increasing pressure from global climate change prompted the research and use of sustainable alternative raw materials. Bioethanol can be effectively employed as (i) fuel for transportation, (ii) substrate for hydrogen generation, and (iii) feedstock for producing commodity chemicals for industrial applications [1]. In recent years, the production of ethanol from fermentation has been increasing until reaching an estimated annual amount in 2020 of more than 120 billion liters [1]. Ethanol is effectively used for producing acetaldehyde, acetic acid, ethylene, and butadiene. All mainstream processes for acetaldehyde production entail the employment of non-renewable energy sources, high operating pressures and temperatures, and large process costs. Photocatalytic processes allow to overcome such drawbacks, due to the use of the solar radiation as energy source and possibly low cost photocatalysts. Photocatalytic oxidation of ethanol in liquid phase is of major interest as it enables (i) direct use of bioethanol from fermentation or ethanol from industrial wastewater and (ii) adoption of mild operating conditions. The system Cu(II)/TiO<sub>2</sub>/UV-A for the selective oxidation of ethanol to acetaldehyde and acetic acid was investigated at varying operating conditions, such as starting cupric ion and ethanol concentrations. As the oxidation process proposed was performed in liquid phase, acetaldehyde recovery by its stripping from the aqueous medium via N<sub>2</sub> bubbling was tested. After acetaldehyde recovery, the possibility of an *in situ* photocatalyst regeneration was assessed. With a view to industrial applications, the safety aspects of photocatalyst regeneration were considered. A mathematical model was developed with the aim of simulating the system behavior and estimating kinetic parameters not available in the literature review.

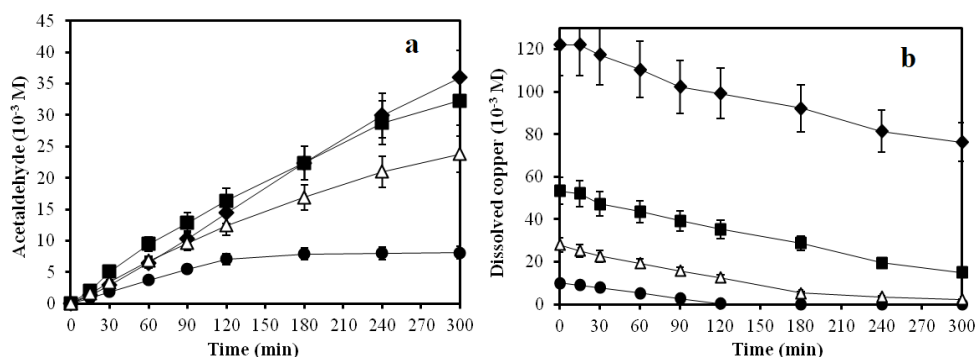
### **2. Methods**

Photocatalytic runs were carried out in an annular glass batch reactor (0.3 L) thermostated at 25 °C and equipped with a magnetic stirrer. A high-pressure mercury vapor lamp was located inside a glass cooling jacket in the center of the reactor and surrounded by the reacting solution. For each run fixed amounts of P25-TiO<sub>2</sub> and CuSO<sub>4</sub>·5H<sub>2</sub>O were added to the mixture. N<sub>2</sub> was previously fed in order to prevent the air inlet into the reactor. In all runs, the pH of the solution was adjusted to 3.0 by means of HClO<sub>4</sub> and constantly monitored. Dissolved Cu concentration was measured through a colorimetric method. Organic concentration was measured by means of HPLC analysis. All the details are reported in a previous study [2]. For stripping experimental run, the photocatalytic reactor was followed by two trapping units containing bidistilled water at pH 3.0 (V=0.3 L) [3].

### **3. Results and discussion**

In a typical photo-oxidation run at high starting ethanol concentration ([Ethanol]=1.0 M;

[Cu(II)]<sub>0</sub>=10·10<sup>-3</sup> M; P25-TiO<sub>2</sub> load=150 mg/L; pH=3.0; T=25°C; P=1 atm), remarkable selectivity toward acetaldehyde production (≈96%) was recorded, while small amounts of acetic acid were collected. The simultaneous photoreduction of cupric ion to zerovalent copper was observed [3]. A wide range of starting cupric ion concentration (10·10<sup>-3</sup>-120·10<sup>-3</sup>M) was explored while fixing the other operating variables. At the end of a typical photo-oxidation run, the aqueous mixture at still high ethanol concentration and with considerable acetaldehyde content was bubbled with a N<sub>2</sub> stream in order to completely separate acetaldehyde by absorbing it in the trap units in series. Almost all acetaldehyde produced upon photo-oxidation (93%) was separated from the aqueous mixture after 120 minutes of stripping. After selective photo-oxidation and stripping, an *in situ* photocatalyst regeneration via zerovalent copper reoxidation was also successfully performed after 180 minutes of air bubbling of the reacting mixture, thus outlining the environmental and economic viability of the process. The flammability of ternary gaseous mixture (ethanol/oxygen/nitrogen) coming out from the reoxidation step was evaluated by employing the triangular diagram along with the data referring to the partial pressures of ethanol and water [3]. According to flammability analysis, the reoxidation procedure proved to be safe. Detailed information on the reaction mechanism and kinetics regulating the system Ethanol/Cu(II)/TiO<sub>2</sub>-P25/pH=3.0 could be found in a previous study [2]. The photo-oxidation process at high ethanol content, as expected for real applications, and varying starting Cu(II) concentrations (10·10<sup>-3</sup>- 120·10<sup>-3</sup> M) was considered for the present kinetic study. As a result of the modelling investigation, the best values of unknown parameters were estimated, such as the rate constant of adsorbed acetaldehyde reaction with photogenerated positive holes and the quantum yield in the UV-A range. As shown in Figures 1 a,b, by comparing experimental and theoretical data of acetaldehyde production (Panel a) and cupric ion reduction (Panel b), the ability of the model to successfully predict the overall system behavior under different operating conditions was proved.



**Figure 1.** Comparison between experimental (symbols) and calculated values (continuous lines). [Ethanol]<sub>0</sub>=1.0 M; TiO<sub>2</sub>-P25 load=150 mg/L; pH =3.0; T=25°C; P=1 atm. [Cu(II)]<sub>0</sub>: 10·10<sup>-3</sup> M (●); 25·10<sup>-3</sup> M (△); 50·10<sup>-3</sup> M (■); 120·10<sup>-3</sup> M (◆).

#### 4. Conclusions

The selective photo-oxidation of ethanol to acetaldehyde in the presence of cupric ion and P25-TiO<sub>2</sub> was studied for the first time in liquid phase, with the aim of maximizing production and recovery of acetaldehyde. An *in situ* photocatalyst regeneration via Cu(0) reoxidation was successfully performed and the safety aspects were evaluated. A mathematical model was developed with the aim of providing a reliable starting point to develop future kinetic analyses on photocatalytic selective oxidation of alcohols in aqueous solution and in presence of metal ions.

#### References

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