

# Gas-phase Photocatalytic Synthesis of Acetaldehyde from Ethanol: Thermodynamic Evaluation and Comparison with Photocatalytic Activity

Vincenzo Vaiano\*, Diana Sannino, Paolo Ciambelli

Department of Industrial Engineering, University of Salerno, Via Giovanni Paolo II 132, 84084 Fisciano (SA), Italy  
 vvaiano@unisa.it

This work is focused on the thermodynamic evaluation as a preliminary step for the photocatalytic partial oxidation of organic compounds aimed to the synthesis of high valued chemicals. The comparison of thermodynamic data with the experimental ones for the partial oxidation of ethanol to acetaldehyde have been discussed and connected to the kinetics of the photoreaction system. Experimental data has shown the influence of the reaction temperature and the contact time in the distribution of the reaction products. Interesting is the control on the products distribution induced by the contact time, which drives towards the thermodynamic expectations, when it is high. The choice of the appropriate contact time in the photocatalytic reaction permits to get the desired product with the highest yield.

## 1. Introduction

Photocatalysis is a research and technological area where a wide number of studies and applications have been developed and takes advantage of the properties of semiconductor materials able to carry out chemical reactions, potentially at very limited cost, because of the presence of photons coming from solar or artificial light (Hoffmann et al., 1995). The strong promotion of oxidation and reduction reactions, without necessity of severe operating conditions, is accomplished by the removing the requirement of expensive and dangerous chemicals causing a reduction of cost and limited safety precautions, satisfying the requisites of a green chemistry process (Hoffmann et al., 1995). This is the reason for which the research is rapidly growing, as demonstrated by the remarkable number of papers published, starting from very few and pioneer works from the seventies (Bickley et al., 1973), as for example regarding the photocatalytic water splitting using UV energy, (Fujishima and Honda, 1972) up to now.

The subject areas are different, the most related to the chemistry and material science, but also to chemical engineering and engineering aspects. Large studies are devoted to environmental science for the purification of gaseous stream (Murcia et al., 2013) and wastewater purification (Vaiano et al., 2014), to H<sub>2</sub> production and to profit of renewable energy, as the solar light. Recently photocatalysis was also regarded as an emerging technology for chemical transformations, responding to the requirements of the sustainable chemistry, since its potentiality to realize cleaner industrial productions (Saini and Singh, 2002). The majority of papers now are focusing on the shifting of photocatalytic activity from UV to visible irradiation, while some interesting papers are rising about the photocatalysis as suitable method for green organic synthesis. Recently, a special issue on the photocatalytic partial oxidation has been published (Sannino et al., 2013a). Wide examinations of the main parameters that control photoactivity, such as chemical composition of the photocatalysts and photoreactors irradiated with solar light have been and are continuously studied. However, the new goal for studying the photocatalytic processes is to try to establish some approaches to their study.

In this perspective, the traditional approach that foreseen a direct kinetics study of the semiconductor photocatalyst have to be integrated. In fact, the synthesis of products of interest for industrial chemistry requires the additional use of thermal energy to be coupled to the light energy, or the integration with

additional operations to have separation, extraction and purification of the produced compounds. A large numbers of studies and evaluations have been published up to now.

However, all these studies never started from a rigorous estimation of the thermodynamics yield of the photocatalytic reactions. This is due, to the obviousness of thermodynamic fate for photocatalytic reactions dedicated to total oxidation of pollutants, because the formation of CO<sub>2</sub>, as it is well known, is widely favoured in mild temperature and pressure, typical of photocatalytic processes.

The situation could be different when partial oxidation products are desired, together with high selectivity requirements, which could constrain the operating conditions of the processes. The thermodynamic evaluation of a reacting system involves the search of most profitable conditions of the intensive variables to maximize the yield towards the desired product.

As it is usually conducted in industrial processes study, the first approach for the reactions occurring in the gas phase consists in the definition of the reaction system and the individuation of the thermodynamic yield of products, with respect to the initial composition, temperature and pressure. Another aspect that is to be considered is to define thermal exchange and thermal duty of the reactions. In photocatalysis, the most used system work at atmospheric pressure, so a first condition is individuated and could be fixed. With reference to the thermal effects, diluted stream are often used, so the heat of reaction developed could be easily controlled and isothermal condition can be achieved. The most of photocatalytic reactors in fact, operate in isothermal and low temperature mode. However, apart from the experimental approach, no thermodynamic evaluation have been performed and reported up to now in the literature.

In this view, this work is focused on the thermodynamic evaluations as a preliminary step for the photocatalytic partial oxidation of organic compounds aimed to the synthesis of high valued chemicals. The comparison of thermodynamic data with the experimental ones for the photocatalytic conversion of ethanol to acetaldehyde will be discussed and connected to the kinetics of the photoreaction system.

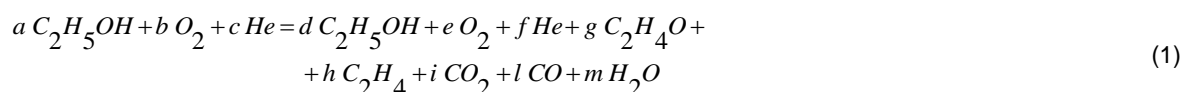
## 2. Experimental

### 2.1 Thermodynamic evaluation

Thermodynamic analysis has been carried out with the Gaseq program, a Microsoft Windows program with a graphic interface. The basic principle of this program is the minimization of Gibbs free energy, considering chemical equilibrium of perfect gases.

Thermodynamic study of the reaction of ethanol has been performed considering as potential products those found in previous works about the photocatalytic selective oxidation of ethanol to acetaldehyde (Sannino et al., 2012). Since water production was observed on specific photocatalysts (Murcia et al., 2012), chemical substances such as ethylene, carbon monoxide and CO<sub>2</sub> have to be considered with together acetaldehyde.

The following general equation can be set:



Taking into account that the photoreactor operates at ambient pressure, the pressure was set to 1 atm while the ratio O<sub>2</sub>/C<sub>2</sub>H<sub>5</sub>OH was equal to 2, being the latter the optimal feeding ratio for obtaining the highest yield of acetaldehyde from previous experimental tests (Sannino et al., 2012). The inlet ethanol concentration and the temperature were allowed to vary and in particular in the following ranges:

- T = 25 - 575 °C ;
- Initial C<sub>2</sub>H<sub>5</sub>OH concentration: 0.2 - 2.0 vol %.

The simulation results were analyzed in terms of ethanol conversion and acetaldehyde, ethylene, CO<sub>2</sub> and CO yield.

The conversion (X) and yield (R) are defined in the following equations:

$$X_{C_2H_5OH} = \frac{n_{C_2H_5OH}^{in} - n_{C_2H_5OH}^{out}}{n_{C_2H_5OH}^{in}} \quad (2)$$

$$R_{C_2H_4O} = \frac{n_{C_2H_4O}^{out}}{n_{C_2H_5OH}^{in}} \quad (3)$$

$$R_{C_2H_4} = \frac{n_{C_2H_4}^{out}}{n_{C_2H_5OH}^{in}} \quad (4)$$

$$R_{CO_2} = \frac{1}{2} \frac{n_{CO_2}^{out}}{n_{C_2H_5OH}^{in}} \quad (5)$$

$$R_{CO} = \frac{1}{2} \frac{n_{CO}^{out}}{n_{C_2H_5OH}^{in}} \quad (6)$$

Where  $n^{in}$  and  $n^{out}$  represent, respectively, the initial and final moles.

## 2.2 Photocatalyst preparation and characterization

For photocatalytic tests, an innovative formulations of photocatalysts (Sannino et al., 2013b), based on  $VO_x/TiO_2$  supported on phosphors particles, were used.

Phosphors (model RL-UV-B-Y; Excitation Wavelength: 365 nm; Emission Wavelength: 440 nm; particles diameter: 5 - 10  $\mu m$ , provided by DB Chemic) coated with  $TiO_2$  was prepared by incipient wet impregnation method. Phosphors sample was added to solution of titanium isopropoxide in isopropanol, dried at 80 °C and calcined in air at 400 °C for 3 h. A second impregnation with an aqueous solution of ammonium vanadate was performed to have  $VO_x/TiO_2$ /phosphors catalysts. The optimized  $TiO_2$  content was 30 wt % (Sannino et al., 2013b) while  $V_2O_5$  nominal loading was 5 wt% based on the  $TiO_2$  loading in  $TiO_2$ /phosphors samples. The preparation method induced the formation of  $TiO_2$  in anatase phase dispersed on phosphors surface (Sannino et al., 2013b) and the addition of  $VO_x$  species on  $TiO_2$ /phosphors composite support determined a decrease in band gap energy from 3.2 up to 2.8 eV (Sannino et al., 2013b). The value of 2.8 eV means that  $VO_x/TiO_2$ /phosphors can be excited by the radiation emitted by phosphors (Sannino et al., 2013b).

## 2.3 Experimental set-up for the evaluation of photocatalytic activity

Catalytic tests were carried out feeding 30 L/h (STP) at inlet ethanol concentration in the range 0.2 - 2 vol % with oxygen/ethanol ratio of 2; temperature and pressure reaction were 100 °C and 1 atm, respectively. The contact time was in the range 22 - 560 ms. The photoreactor was a two-dimensional fluidized reactor whose geometrical characteristics are reported in (Palma et al., 2010). This photoreactor configuration allowed to avoid the deactivation phenomena that typically occurs in gas-phase fixed bed photoreactors (Sannino et al., 2011). The photocatalytic fluidized bed reactor was illuminated by two UVA-LEDs modules positioned in front of the reactor pyrex windows (light intensity: 90 mW/cm<sup>2</sup>) (Palma et al., 2010). Each module consisted of 40 UV-LEDs emitting at 365 nm. To improve fluidization of photocatalysts, 20 g of glass spheres (Lampugnani) were mixed with samples. The gas composition was continuously measured by an on-line quadrupole mass detector (TraceMS, ThermoElectron) and a continuous CO-CO<sub>2</sub> NDIR analyser (Uras 10, Hartmann & Braun).

## 3. Results and discussion

At the run starting time, the feed reaction gaseous mixture is sent to the reactor in dark conditions for a time depending on the restoring of the value of the inlet ethanol concentration. In such way, only adsorption equilibrium of ethanol on the catalyst surface occurred, since in the absence of light, no reaction products were observed during or after the ethanol dark adsorption at set reaction temperature. This behavior well evidences that at 100 °C and in the absence of light, no reaction products were observed during or after the ethanol dark adsorption. As a consequence no selective ethanol oxidization occurs by thermal catalysis at reaction temperature and in the used operating conditions. After adsorption step, UVA-LEDs were switched on and the ethanol outlet concentration decreased during the time reaching a steady state value. The reaction products were analysed in the outlet stream determining the presence of acetaldehyde with together and CO<sub>2</sub> and ethylene. The typical behavior was reported in (Sannino et al., 2013b). Figure 1 shows the comparison between the experimental data and the expected values at equilibrium in terms of ethanol conversion with together acetaldehyde, ethylene and CO<sub>2</sub> yield at a temperature of 100 °C. The experimental results are reported as function of initial concentration of ethanol and at fixed contact time (22 ms). Ethanol conversion decreased with the increase of inlet alcohol concentration, being however always below the thermodynamic evaluation. It's relevant to consider that in these operating conditions, photon flux is largely abundant with respect to the request of the studied photoreaction, so is not a limiting condition (Palma et al., 2010). However, the curve agrees with the expected trend towards the thermodynamic conversion. The same

behavior is not obtained for the acetaldehyde yield. Surprisingly, acetaldehyde appears strongly superior to the thermodynamic expectations. This behavior is, however, common in industrial processes, where some catalytic reactions are conducted in no-equilibrium conditions. A different behavior is observed for ethylene and CO<sub>2</sub>; the thermodynamic evaluation indicates high values of ethylene and CO<sub>2</sub> yield, while the results concerning the photocatalysis show quite negligible values for CO<sub>2</sub> and ethylene yield, very lower than thermodynamics estimation.

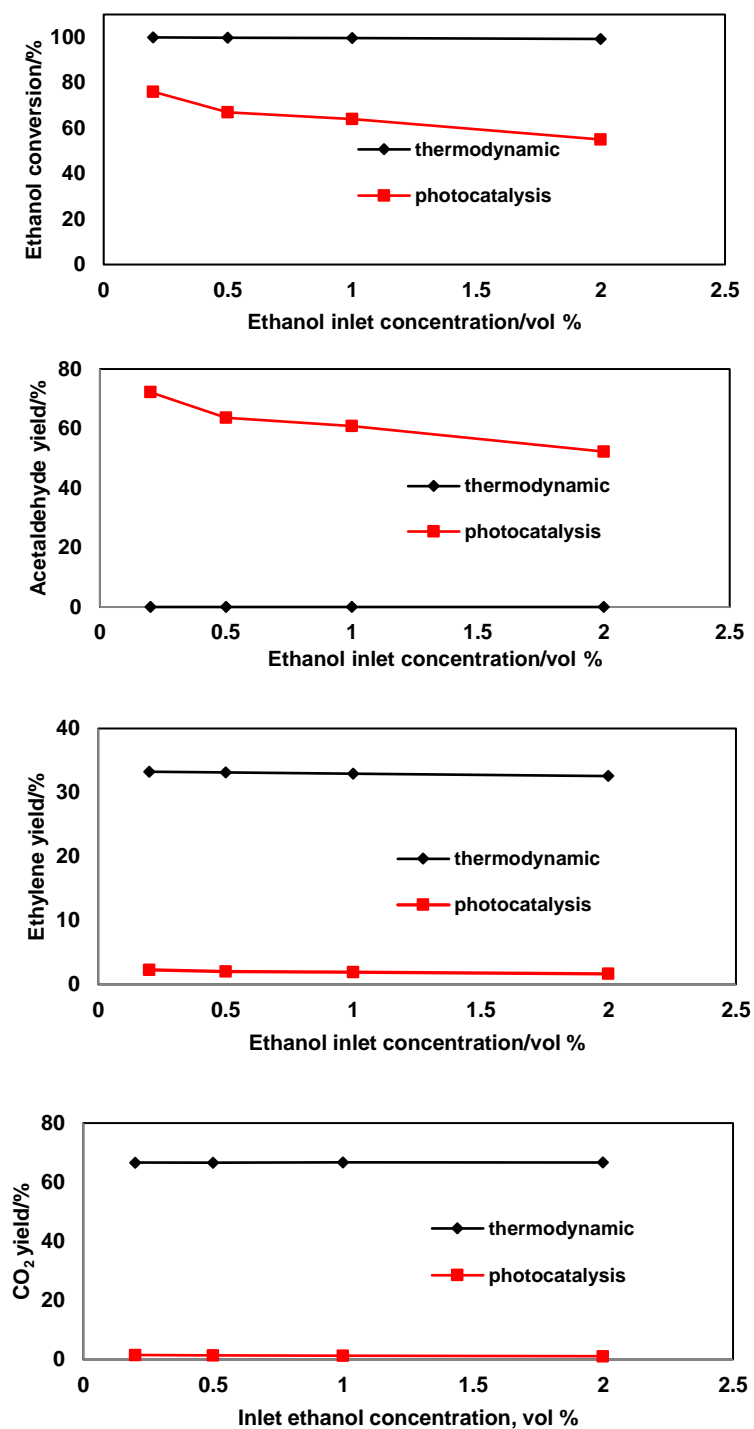


Figure 1: Ethanol conversion, acetaldehyde ethylene and CO<sub>2</sub> yield as a function of inlet ethanol concentration; contact time: 22 ms; reaction temperature: 100 °C.

This result emphasizes that in photocatalysis, the action of UV light in combination with the visible radiation emitted by the phosphors and thermal effects, manage to enhance the kinetics of formation of acetaldehyde beyond the limits imposed by thermodynamics.

These results require nevertheless to be validated to exclude any source of experimental errors. To this purpose, tests at different contact times were performed to investigate the effect of this last parameter on the conversion of ethanol and products distribution. Figure 2 shows the steady state values of ethanol conversion and products yield. Also with different contact times, the most significant products formed are acetaldehyde, ethylene, and carbon dioxide. As it can be seen from the results obtained with a contact time equal to 22 ms, the system is still not at equilibrium. By increasing the contact time, the conversion of ethanol increases up to reach the equilibrium value corresponding to its total conversion. Moreover, the shifting toward thermodynamic conditions was shown at a contact time of approximately 560 ms. In this condition, the acetaldehyde, ethylene and CO<sub>2</sub> yield become coincident to the corresponding equilibrium values.

The behavior of the products yield presented in Figure 2 can help elucidate the global chemical reaction mechanism for the photocatalytic oxidation of ethanol on VO<sub>x</sub>/TiO<sub>2</sub>/phosphors. In particular, the obtained experimental results support the following global reaction scheme:



In addition, ethylene is formed by ethanol dehydration reaction.

In summary, these results highlight the potentiality of the photocatalytic system in modulating the yield to the desired product by suitably adjusting the contact time. In particular, low contact times allow to maximize the formation of acetaldehyde.

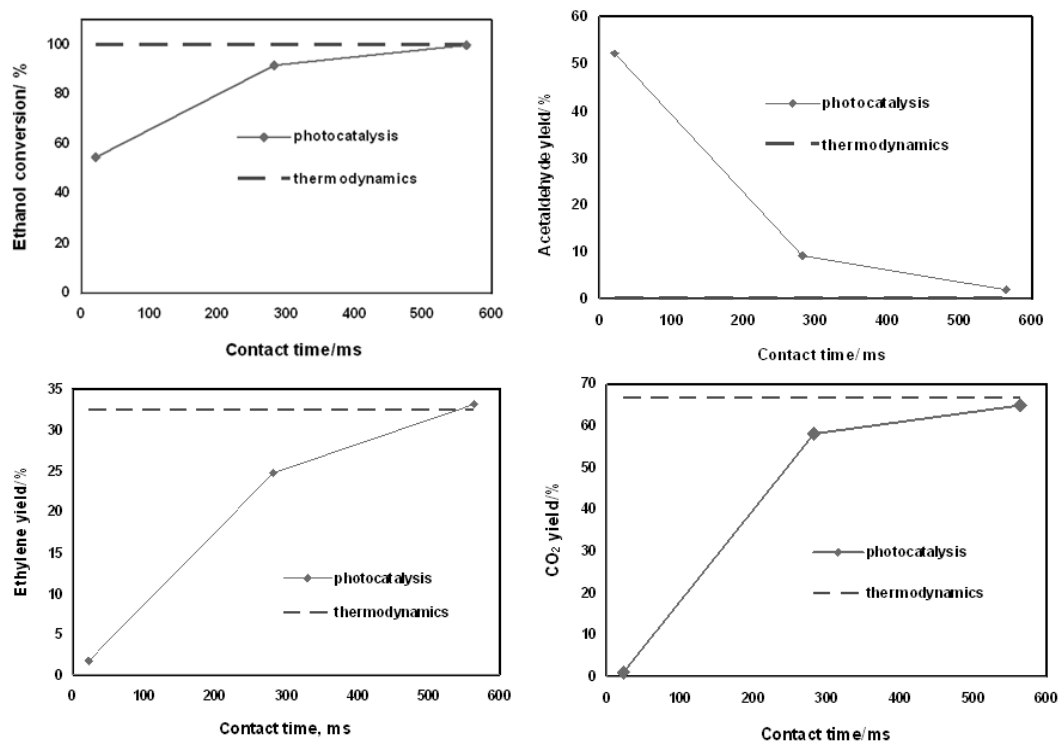


Figure 2: Ethanol conversion, acetaldehyde ethylene and CO<sub>2</sub> yield as a function of contact time; ethanol inlet concentration: 2 vol %; reaction temperature: 100°C

#### 4. Conclusions

The comparison of thermodynamic data for the photoconversion of ethanol to acetaldehyde with the experimental data has shown the influence of the temperature, and the contact time in the modulation of the reaction products.

The Increase of the temperature together with irradiation brings several benefits to partial oxidation increasing the transferring of the expected product in gas phase, and so increasing the turnover of molecules on the active sites for their transformations.

Interesting it is the control on the products distribution induced by the contact time, which drives to the thermodynamic expectations if it is high. The set-up of the contact time permits to get the desired product with the highest yield.

The behavior of the photoreaction system analyzed resembles that of conduction of important industrial reaction, such as industrial catalytic production of nitric acid. These results could be obtained only when the absence of irradiation limitations is achieved.

## References

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