

Oxalic Acid Photoreforming With Simultaneous Hydrogen Evolution: Kinetic Aspects

Yamen AlSalka¹ and Detlef W. Bahnemann^{1,2}

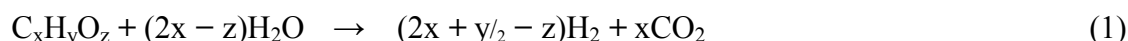
¹ *Leibniz Universität Hannover, Institut für Technische Chemie, photocatalysis & nanotechnology, Callinstr. 3, D-30167 Hannover, Germany*

² *Saint-Petersburg State University, Laboratory “Photoactive Nanocomposite Materials” (Director), Ulyanovskaya str. 1, Peterhof, Saint-Petersburg, 198504 RUSSIA*

E-mail: alsalka@iftc.uni-hannover.de / bahnemann@iftc.uni-hannover.de

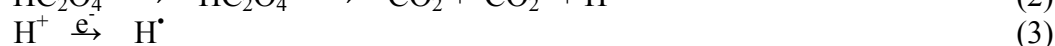
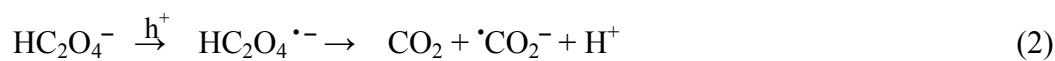
Clean energy systems are increasingly required to meet the growing global energy demand, to overcome the environmental problems of our modern society, as well as to adapt more sustainable energy solutions. Semiconductor nanoparticles (NPs) have been used and optimized for many applications such as hydrogen production and energy conversion in solar cells.^[1] Moreover, the ability to combine photocatalytic water splitting and the treatment of industrial effluents may be regarded as an added value for this technique.^[2]

Adding sacrificial reagents, which will undergo the photoreforming process, has been shown to improve the photocatalytic hydrogen evolution.^[3] Photoreforming could be considered as an intermediate process between photocatalytic water splitting and photo-oxidation, where the organic substance will be oxidized on the photocatalyst surface, whereas water would be reduced to form H₂ as shown in equation (1).^[4]



Photoreforming of oxalic acid has been investigated in detail under inert and pH-controlled conditions employing the pH-stat technique to maintain the pH constant during the experiments. The photocatalytic degradation measurements were performed by two analytical methods: potentiostatically by means of a pH-stat and chromatographically by high-performance ion chromatography (HPIC). In addition, the amount of hydrogen gas evolution was determined by gas chromatograph (GC) equipped with a TCD detector. Self prepared bare titanium dioxides (TiO₂) in anatase form, as well as loaded with platinum NPs (0.25 wt% Pt/TiO₂) have been used as photocatalysts during the photocatalytic tests.

Using bare TiO₂, the photoreforming of oxalic acid under inert conditions was about 73 times slower than its photocatalytic-oxidation in the presence of oxygen. Although the degradation of oxalic acid followed pseudo-first order kinetics in both cases, its degradation under inert conditions was accomplished through two steps, a fast step followed by a slower one. Formic acid was also formed following two step pseudo-first order kinetics as a result of oxalic acid photodegradation according to equations (2-4) through the photo-Kolbe reaction.



The presence of platinum as co-catalyst significantly 9-fold enhanced the photoreforming of oxalic acid but did not affect its degradation kinetics. The formation of formic acid was faster compared to that of bare titanium dioxide, where an increase in its concentration was noticed during the degradation of oxalic acid before it underwent a fast degradation accompanied by the degradation of the remaining quantity of oxalic acid. A complete degradation of both, oxalic and formic acid was achieved after about 240 min of irradiation. The photocatalytic hydrogen formation was followed pseudo-first order kinetics, and its evolution was kinetically related to the degradation of oxalic acid. The contribution of oxalic acid in the photocatalytic formation of hydrogen gas was calculated based on the ratio between the total moles of formed hydrogen gas to those of consumed oxalic acid.

Acknowledgement: We gratefully acknowledge the financial supported from “Leadership for Syria” program funded by the Deutscher Akademischer Austauschdienst (DAAD) and the Federal Foreign Office.

References:

- [1] Friehs, E., et al., Journal of Photochemistry and Photobiology C: Photochemistry Reviews, **2016**, 29, 1
- [2] Ahmad, H., et al., Renewable and Sustainable Energy Reviews, **2015**, 43, 599
- [3] Ma, Y., et al., Chemical Reviews, **2014**, 114, 9987
- [4] Puga, A.V., Coordination Chemistry Reviews, 2016, 315, 1