Photocatalytic hydrogen production using TiO_2-based materials and different sacrificial agents

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1. Introduction –

In an increasingly technological and industrialized world, global energy consumption is not going to decrease. According to the BP Statistical Review of World Energy [1], in 2017 the largest increase was in the consumption of natural gas followed by that of renewable energy and then oil. Renewable power grew by 17% mostly due to wind energy. However, renewable energies (including hydroelectric energy, wind, solar, biomass and geothermal) only constitute 10.4% of global energy consumption. The development of renewable energy has been boosted by the implementation of scientifically backed regulations, and its role is ever more relevant. But its deployment has been slow. Unfortunately the increase of energy use is not being met by renewables. In addition, the sources of renewable energies are intrinsically variable but recent developments in energy storage have made this less of a problem [2]. An example used for decades is using the energy excess to pump water back behind hydroelectric dams. The US has 96% energy storage capacity in the form of pumped hydroelectric storage. There are other alternatives such as thermal storage, hydrogen, compressed air. Hydrogen is a zero carbon fuel and can be generated by a very simple process. For instance, among the Advanced Oxidation Processes, the Heterogeneous Photocatalysis developed in anaerobic conditions is able to create hydrogen from natural or artificial **Image 1. Solar** radiation sources. The fundamentals of Heterogeneous Photocatalysis are **photoactivity reactor** very basic: radiation with enough energy is absorbed by the semiconductor particles causing the promotion of electrons from the valence band to the conduction band. The photogenerated charges (electron and hole) migrate to the surface of the catalyst and that is where redox reactions occur. The hydrogen is produced from the reduction of hydrogen ions. TiO_2 is the material most used in this process because of its chemical stability. The original and more challenging goal of the Heterogeneous Photocatalysis is to get the hydrogen from the photosplitting of water molecules. However, the yield obtained in this process is insignificant and a plausible alternative is the photoreforming of organic compounds. The advantages of photoreforming are even larger because those organic compounds could come from waste material such as glycerine from biodiesel production, or formalin widely used for tissue conservation.

2. Experimental –

Tests were performed in a home-made design reactor. The UV source was a 60W Philips Solarium HB175 equipped with four 15W Philips CLEO fluorescent tubes with emission spectrum from 300 to 400 nm (maximum around 365 nm). The photoreactor was operated in continuous mode at 1 bar and room temperature. A nitrogen flow, controlled with mass-flow measurement systems, was used to displace the

hydrogen from the photoreactor headspace towards the gas chromatograph (GC) instrument measuring system provided with a thermal conductive (TCD) detector. When it was necessary to adjust pH, diluted H_2SO_4 and/or NaOH were used.

Initially a screening of commercial catalysts and other home-made catalysts was carried out [3]. Commercial catalyst were chosen by being widely used in photocatalysis due to their high activity, such as: Hombikat UV100, Millenium PC100, Kronos vlp7000 KR), Aeroxide P25 (P25) and Kemira 625. The catalysts were deeply characterized by different techniques: BET, XRD, TEM, SEM-EDX, FTIR, UV-vis Reflectance Diffuse Spectra and aggregate size.

Selected catalysts were modified with the incorporation of noble metal particles of platinum and gold on the surface by the photodeposition method from chloroauric acid trihydrated ($HAuCl_4 \cdot 3H_2O$) and hexachloroplatinic acid hexahydrated ($H_2PtCl_6 \cdot 6H_2O$) respectively [4,5]. The quantity of the metal deposit varied in the range 0.2-6.0 wt% for gold and 0.5-2.1 wt% for platinum.

The most efficient catalysts were consequently tested using different pH values, sacrificial agents and concentrations of sacrificial agents [6]. Finally some experiments were carried out using solar radiation and externally sourced residues - formalin residue from Veterinary School of the University of Las Palmas de Gran Canaria and glycerine residue from an industrial biodiesel plant in Gran Canaria (Recursos y Residuos Ganaderos s.c.p.).

3. Results and Discussion –

Some characteristics of the most effective commercial catalysts are summarized in Table I. Kronos vlp7000 exhibited the largest hydrogen production reaching a maximum of 21.90 $\mu mol \cdot h^{-1}$. Hydrogen obtained for Pt modified catalysts was >100 times higher than in its absence and in this case, the best catalyst was Pt-P25, with 2800 $\mu mol \cdot h^{-1}$ at 2.1 wt% Pt. However in the case of gold the higher production was showed by Kronos vlp7000, 1082 $\mu mol \cdot h^{-1}$ for 2.0 wt% Au.

Table I. Characteristics of commercial Aeroxide P25 and Kronos vlp7000.

	%anatase	**%rutile**	**anatase size/ nm**	**rutile size/ nm**	**band gap/ eV**	**BET surface/ g/m^2**	**pore volume/ cm^3/g**
P25	82	18	23	44	3.18	48.6±0.1	0.176
KR	100	0	7	0	3.24	259±2	0.392

Different alcohols were tested as sacrificial agents: methanol, ethanol, ethyleneglycol and glycerol in a concentration range from 1.22 M to 100% v/v. The concentrations and maximun flow obtained for each sacrificial agent are shown in Table II. In the catalyst reuse tests, Kronos vlp700 showed shorter cycles to consume 0.011 M sacrificial agents that those showed by Aeroxide P25.

Table II. Maximum flow of hydrogen and corresponding concentration for different sacrificial agents and Kronos vlp700-2.1 wt% Pt.

Sacrificial agent	**Concetration/M**	**Maximum flow/ $\mu mol \cdot h^{-1}$**
methanol	7.34	1665
ethanol	4.89-7.34	1400
ethylene glycol	1.22	1347

glycerol	1.22-8.53	1300

In the solar tests, hydrogen obtained up to a total accumulated energy of 44.7 $W \cdot h \cdot m^{-2}$ was:
4183.87 μmol for glycerol (7.34 M), 3428.7 μmol for methanol (7.34 M) and 1029.4 μmol for ethanol (7.34 M). The hydrogen production did not follow the tendency observed in the Table II due to the variation of the instantaneous irradiance.
In the case of real externally sourced residues, a decrease in hydrogen production was observed that could be related to the residue matrices.

4. Conclusions –

Heterogeneous Photocatalysis is an eco-friendly method of obtaining hydrogen by eliminating organic compounds from residual effluents. Preliminary studies have shown that it is also possible to obtain it through solar radiation although further research is needed into the production of hydrogen in this way, and the optimization of reactor designs.

5. Acknowledgements –

We are grateful for the funding of the Spanish Ministry of Science and Innovation and Spanish Ministry of Economy and Competitiveness for their financial support through the Project GESHTOS (IPT-1200002010-033) and the Infrastructure Project UNLP10-3E-726.

6. References –

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