



Photocatalytic Hydrogen Production using Ethanol as Sacrificial Agent from Gas and Liquid Phases on Reduced Graphene Oxide-TiO₂- Pt nanocomposites

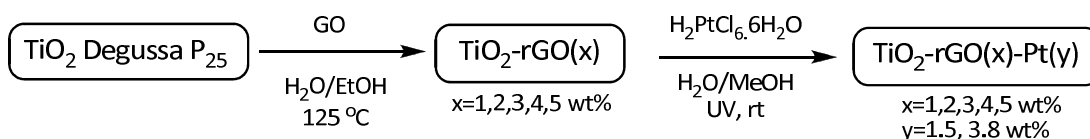
M. A. Esteves¹, F. Fresno², V.R. Fernandes¹, V.A. de la Peña O'Shea², C.M. Rangel^{1*}
LNEG_Laboratório Nacional de Energia e Geologia, Paço do Lumiar, 22 1649-039 Lisboa, Portugal
Institute IMDEA Energy, Avda. Ramón de la Sagra 3, 28935, Madrid, Spain
*carmen.rangel@lneg.pt

Introduction

Various strategies such as heterostructuring, crystal/textural modifications and band gap engineering, have been applied to the improvement of the photocatalytic activity of Titania for hydrogen production from water splitting. In this work deposited Pt on TiO₂ is used as electron trap to suppress charge recombination. To reinforce this effect, composites with graphene oxide (GO) have been prepared, exhibiting promising photocatalytic performance for both hydrogen generation and the degradation of ethanol added as hole scavenger. Photocatalytic reactions were conducted in gas and liquid phases.

Results and discussion

TiO₂-rGO(x)-Pt(y) photocatalysts were prepared by a simple two step process:



Photocatalysts TiO₂-rGO(x)-Pt(y) (x=0-5 wt%; y=1.5, 3.8 wt%) were obtained by platinum doping of the TiO₂-rGO(x) nanocomposites, previously prepared by an hydrothermal method, using a photodeposition method. First, the TiO₂-rGO(x) nanocomposite was dispersed in a 10% (v/v) methanol aqueous solution by ultrasonication. Then, the suspension was transferred to a photochemical borosilicate glass reactor equipped with a double quartz immersion well and the appropriate amount of hexachloroplatinic acid added. The mixture was purged with N₂ for 15 min and then subjected to UV irradiation, for 3 h, using a 450 W mercury-vapor lamp, at room temperature. Characterization of the catalyst has shown platinum nanoparticles in the composite to be well distributed (TEM) and evidenced the reduction of graphene oxide in the process (FTIR) as well as band gap narrowing of TiO₂ (UV-vis diffuse reflectance spectroscopy) [1]. The catalysts were used under UV light in the photogeneration of hydrogen using ethanol as sacrificial agent.

Selected optimal operational conditions for TiO₂-rGO(3%)-Pt(3.8%) have given place to very high initial rates of hydrogen production with values of ~560 mmolh⁻¹g_{cat}⁻¹ (for 5 M ethanol solutions with initial pH of 7, 40 °C), but typical graphs show two slopes (hydrogen production rates) for data acquired along 6 hours irradiation time, where the initial high rate reduces to 66 mmolh⁻¹g_{cat}⁻¹. Variation of the gas production rates is associated to drastic pH decrease that reach values of 3.3 at the end of the experiment and to adsorption of intermediates that produces catalyst poisoning. Regeneration of the catalyst has been approached using thermal and chemical treatments, both being effective in the removal of adsorbed reaction products responsible for catalyst deactivation.



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Gas chromatography shows hydrogen as the main product (above 95%) with remaining components being CO and CH₄ and minor amounts of CO₂, C₂H₆ and C₂H₄. Analysis of the liquid phase points towards the presence of acetaldehyde as the main reaction product.

H₂ production was also measured in a gas phase continuous reactor by previously bubbling an Ar flow through a mixture of H₂O:CH₃CH₂OH (10:1) at 60 °C. The sample was irradiated using two UV lamps (365 nm) of 6 W. Obtained rates are comparable with those obtained in second slope in the liquid phase experiments. Product analysis was performed using a mass spectrometer. In addition to H₂ (Figure 1), acetaldehyde and CO₂ (not shown) were also detected as products. The experiments were performed in three on/off cycles in order to evaluate the catalyst stability.

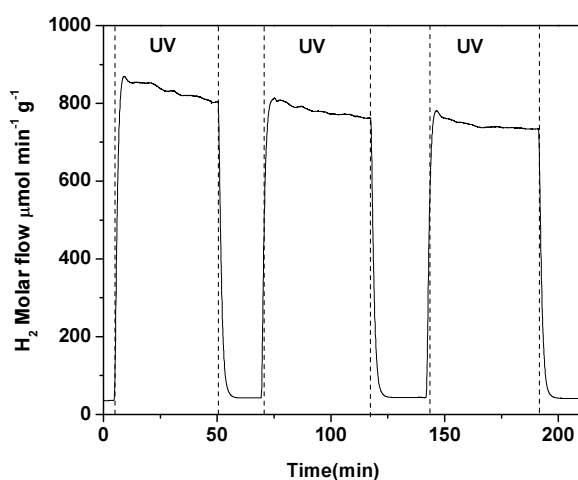


Figure 1. H₂ evolution using TiO₂-rGO3%-Pt3.8% catalyst from the gas phase.

Conclusions

TiO₂-rGO(3%)-Pt(3.8%) catalyst is shown to be an active photocatalyst for the production of hydrogen, using ethanol as sacrificial agent, exhibiting very high rates both in gas and liquid phase reactions. Variations in the gas production rates in the liquid phase are associated to drastic pH decrease and to adsorption of intermediates that cause catalyst poisoning. Regeneration of the catalyst using thermal and chemical treatments have been approach with good preliminary results, both being effective in the removal of adsorbed reaction products responsible for catalyst deactivation, allowing catalyst reutilization.

Acknowledgements

This research was supported by Project “PEMFC-SUDOE” - SOE1/P1/E0293, which is co-financed by the European Regional Development Fund in the framework of the INTERREG SUDOE programme.

References

[1]Paula Ribao, M.Alexandra Esteves, Vitor R. Fernandes, Maria J. Rivero, Carmen M. Rangel, Inmaculada Ortiz, Int. J. Hydrogen Energy, 2018. DOI: 10.1016/j.ijhydene.2018.09.148.