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Glycerol electrooxidation in alkaline media on platinum surfaces modified by bismuth.

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Abstract
We studied the glycerol electrooxidation reaction (GEOR) on Pt surfaces modified by Bi adatoms to understand the effect of catalyst strucutre on the activity and selectivity. This investigation was performed using a combination of electrochemical (cyclic voltammetry), chromatographic (HPLC) and spectroscopic (FTIR) techniques. Our results show that the presence of Bi blocks the reaction pathways that lead to CO formation, a poisoning intermediate, and increase the production rate of glyceric acid.

Key words:
Electrooxidation, Platinum, Bismuth.

Introduction

The growing of the biodiesel industry has led to a surplus in the glycerol (GlOH) available on the market, since it is a co-product during biodiesel production. This caused a significant price drop, leading many research groups to investigate its chemical valorization[1]. In this context, the electrochemical oxidation is an option to this goal.
The electrooxidation offers the advantages of being performed at room temperature and ambient pressure, and the electrocatalysts can be easily modified[2].
In this context, we modified Pt, a common electrocatalyst, by depositing Bi adatoms on its surface, and investigated the effects of this modification on the GEOR in alkaline media.

Results and Discussion

The activity of Pt towards the GEOR was investigated using cyclic voltammetry (image 1). The Bi modification was performed by both partially covering the electrode surface, and directly adding Bi^{3+} ions to the electrolyte. Our results show that the highest activity (current) of the Pt-Bi catalyst was after addition of 10^{-5} M Bi_2O_3 to the electrolyte containing GlOH in alkaline media.

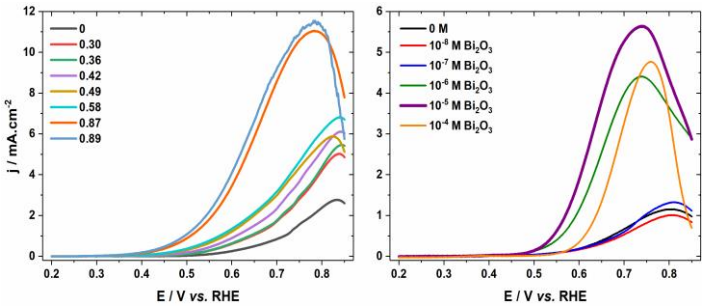

Image 1. (left) Positive scan of the 1st cycle of the GEOR on Pt modified by partial Bi coverage, as indicated on the inset; (right) Positive scan of the 10th cycle of the GEOR on Pt, by adding varying amounts of Bi_2O_3 (0 – 10^{-4} M) to the electrolyte. Base electrolyte is 0,1 M NaOH + 0,1 M GlOH, scan rate is 10mV.s^{-1}.

Product characterization was performed by *in-situ* FTIR on the Pt and Pt-Bi catalysts (image 2). After Bi modification, no bands associated with CO adsorption on Pt were observed, and the band related to carbonate, corresponding to the GlOH total oxidation, was reduced.

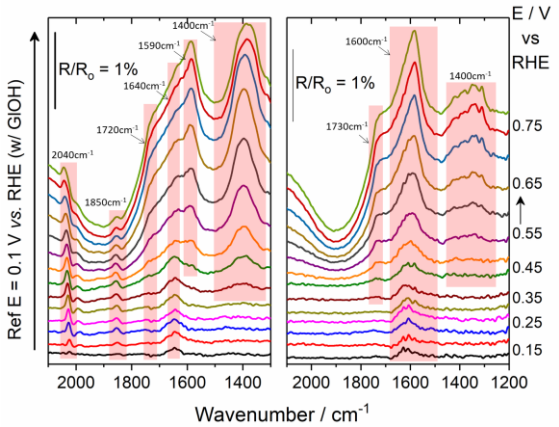

Image 2. Potential-dependent FTIR spectra for the clean (left) and Bi-modified (right) Pt electrodes. Electrolyte composition was 0,1 M NaOH + 0,1 M GlOH, with 10^{-5} M Bi_2O_3 in the Pt-Bi catalyst, using a sweep rate of 2 mV.s^{-1}.

Further investigation with HPLC (image 3) revealed that the Bi-modification improved the production rate of glyceric acid by sevenfold.

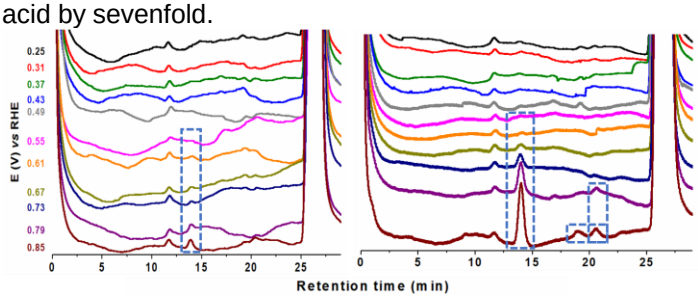

Image 3. Potential-dependent chromatograms for the clean (left) and Bi-modified (right) Pt electrode.

Conclusions

The addition of bismuth on the Pt causes a fivefold increase in the current density in the GEOR. The experiments using HPLC and in-situ FTIR demonstrated that the presence of bismuth inhibits the formation of CO (poisoning intermediate) and favors the formation of glyceric acid.

Acknowledgements

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[1] Ciriminna, R. et. al. *Eur. J. Lipid. Sci. Technol.* **2014**, 116(10), 1432.
[2] Kwon, Y. et. al. *Top. Catal.* **2014**, 57, 1272.