Electrooxydation d'alcools C2 et C3 sur catalyseurs à base de Ni caractérisés par spectrométrie de masse en temps réel.

Electrooxidation of C2 and C3 alcohols on Ni-based catalysts characterized by real-time mass spectrometry.

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Classement du sujet : électrochimie, chimie des matériaux, spectrométrie de masse

Descriptif du sujet :

The search for alternatives to fossil fuels is decidedly addressed by the scientific community due to the unavoidable depletion of the reserves and the umbridled rise of CO_2 gas emissions on a global scale. In this context, green H_2, obtained from renewable energies without CO_2 emissions, will play a key role as an energy vector in the future decarbonized energy systems. One of the most promising H_2 technologies is the water electrolysis at low temperature (<100ºC) in an electrochemical cell to obtain H_2 (on the cathode) and O_2 (on the anode).[1] However, oxygen evolution reaction (OER) has thermodynamic and kinetic limitations that must be overcome to make this technology competitive. In this project, **the traditional OER, from H_2O, will be replaced by less-energy intensive anodic reactions, from organic molecules, to decrease the H_2 production cost**. Besides, the objective is not to fully oxidize the organic molecules into CO_2 but **to perform their selective oxidation to valuable products**.[2] C2 alcohols (e.g., ethanol, ethylene glycol) and C3 alcohols (isopropanol, glycerol) have been selected as model organic molecules. The most active anodes reported in literature are based on noble metals like Pt or Pd.[3] In this project, to perform the electrooxidation of the different organic molecules, **Nickel has been selected as a non-noble metal anodic catalyst**, which will require an **alkaline electrolyte (14 > pH > 11)**.

One of the main challenges in all the research works on organic molecules electrooxidation lies on the control of the catalyst selectivity, due to the complex reaction mechanisms taking place and on the wide variety of reaction products and other degradation molecules that may be obtained. In literature, only gaseous products are typically on-line analyzed (H_2 from the cathodic side; O_2, CO, CO_2 from the anodic side).[4,5] Most of the anodic products are liquid under standard conditions and they are usually quantified by collecting samples from the anodic electrolyte in the course of the electrochemical reaction and analyzing them ex-situ by HPLC or GC-MS.[6] **For the first time, the electrooxidation reactions**

of different alcohols will be studied on Ni-based catalysts with the real-time characterization of the anodic products by mass spectrometry.

For this purpose, **different Ni-based catalysts (monometallic and doped with other transition metals like Fe, Co, Cu or Mn) will be synthesized and tested for alcohols electrooxidation, and a customized mass spectrometry facility will be designed, set-up and optimized to on-line assess the catalytic activity and selectivity as a function of different parameters (applied potential, pH and temperature)**. Many components will be customized, including the electrochemical cell, the sampling system, the gas/liquid separator, the nebulizers and the mass spectrometry detectors among others. The C2 and C3 molecules will be studied in the order of lower-to-higher complexity from the point of view of number of alcohol groups and products volatility. First, the oxidation of monoalcohols (ethanol and isopropanol) and ethylene glycol will be studied, since all the main products are highly volatile (boiling point lower than 120ºC), i.e., formic acid, acetic acid, acetaldehyde, glycolic acid, glycolaldehyde, acetone. Then, glycerol electrooxidation will be studied, where the real-time MS will be specially challenging, since some of the products have a boiling point slightly above 200ºC (glyceroaldehyde, dihydroxyacetone, hydroxypyruvic acid) and others even higher than 400ºC (glyceric acid, mesoxalix acid, tartronic acid).

References

[1]K. Zeng, D. Zhang, Prog. Energy Combust. Sci. 2010, 36, 307.

[2]C. Coutanceau, S. Baranton, Wires Energy Environ. 2016, 5, 388.

[3]M. Simoes, S. Baranton, C. Coutanceau, ChemSusChem 2012, 5, 2106.

[4]N. Grimaldos-Osorio, F. Sordello, M. Passananti, P. Vernoux, A. Caravaca, J. Power Sources 2020, 480, 228800.

[5]L. Han, J. González-Cobos, I. Sánchez-Molina, S. Giancola, S.J. Folkman, P. Tang, M. Heggen, R.E. Dunnin-Borkowski, J. Arbiol, S. Giménez, J.R. Galán-Mascarós, ACS Appl. Energy Mater. 2020, 3, 9198.

[6]Y. Xie, Z. Zou, N. Yang, G. Zhao, Y. Xie, Z. Zhou, G. Zhao, N. Yang, Green Chem. 2014, 16, 3778.

Exigences des candidats :

* Master en chimie, physico-chimie, catalyse ou électrochimie avec :
  - de fortes connaissances en physico-chimie des matériaux
  - des connaissances sur les techniques d'analyse chimique notamment la spectrométrie de masse
  - des connaissances en catalyse et électrocatalyse
* Bon niveau de français et d'anglais
* Motivation et autonomie