

Electrochemical Behavior of Organics Oxidation on Palladium-Based Nanocatalysts Synthesized from Bromide Anion Exchange

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Introduction

Understanding the mechanism and kinetics of the organics oxidation reaction is important for the optimization of fuel cell performance at low temperatures. Glycerol and glucose are two attractive renewable molecules usable as fuels in various potential applications in transportation and portable electronic devices. Their other issue could be the cogeneration of energy (fuel and hybrid biofuel cells)^{1, 2} and chemicals. The latter further concerns their partial oxidative transformation without C–C bond cleavage which leads to added value reaction products. Palladium-based catalysts were found to be active towards the oxidation of these organics in alkaline medium. Nickel, silver and gold as co-catalysts were added to the material composition to decrease the palladium amount and to obtain beneficial synergy effects during the oxidation of glycerol and glucose. Carbon monoxide which is one of the common intermediates observed in such organics oxidation was used as model molecule to characterize the electrochemical activity of the different bimetallic electrode materials prepared from a soft chemical approach free from surfactant molecule.

Experimental

PdM/C (M = Ag, Ni, Au) materials with different atomic compositions were synthesized from the bromide anion exchange (BAE) method.³ They were characterized physicochemically by differential and thermogravimetric analysis (DTA/TGA), X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM). The electrochemical behavior of the anode catalysts was performed by CO stripping and Cyclic Voltammetry (CV). Chromatographic analysis (HPLC) of electrolytic solutions and in situ Fourier transform infrared (FTIR) spectroscopy experiments were carried out to determine the intermediates and the final products resulted in the anodic conversion of the organic compounds.

Results and Discussion

The powders of carbon supported Pd-based nanomaterials were analyzed by DTA/TGA to determine the metal loading. The expected weights were obtained for each sample. This is maybe related to the soft and clean BAE method which does not involve any organic compound as surfactant or stabilizer compared with water-in-oil microemulsion and polyol methods. From the physicochemical characterizations a good dispersion of the nanoparticles on carbon Vulcan XC 72R were obtained (Figure 1a). Particles sizes of 3 to 6 nm for PdAg/C, PdNi/C and PdAu/C were estimated from XRD patterns. The electrochemical activity of the different nanomaterials was first performed in alkaline medium by CO stripping where the shift of the CO oxidation peak was associated with the nature of the co-catalyst in the bimetallic electrode (Figure 1b). As CO can be adsorbed at the lower size gold particles, the surface area of the PdAu/C catalyst was determined from the desorption peaks of Pd and Au oxides. These electrochemical

investigations coupled with in situ IR reflectance spectroscopy allowed to determine that the adsorption modes of CO on Pd-based materials depend on the electronic structure and the geometry of the particles. Linear CO chemisorbs at atoms located on corners and edges, while the bridge-bonded CO adsorbs mainly on the atoms with high coordination numbers, particularly on (100) and (111) faces. Further to the electrochemical behavior of glucose (Figure 1c) and glycerol investigated with cyclic voltammetry and spectroelectrochemistry, long-term electrolyses were carried out in a two-compartment cell. The oxidation potential was set as function of the shift of the oxidation peak and the nature of the co-catalyst. Otherwise, the reaction production analyzed by ionic and isocratic chromatographies strongly depends on the nature of the nature of the co-catalyst in the Pd based bimetallic material.

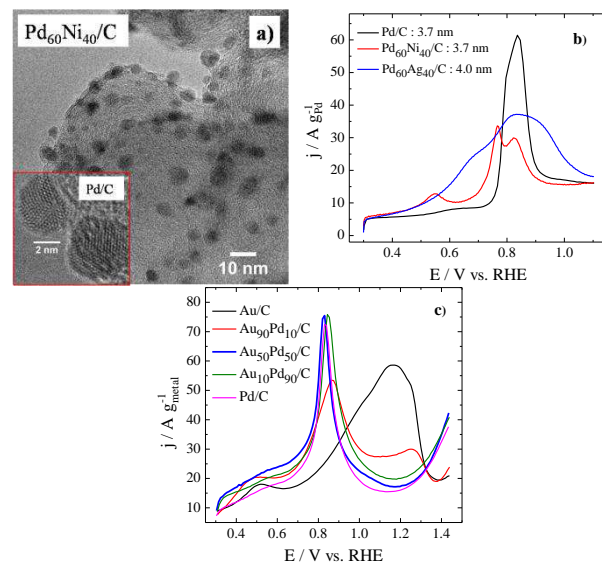


Figure 1: a) TEM image of 30 wt. % Pd₆₀Ni₄₀/C and in inset, HRTEM of 30 wt. % Pd/C. b) CO stripping on 30 wt. % Pd-based catalysts recorded in 0.1 mol L⁻¹ NaOH at 20 mV s⁻¹. c) Polarization curves of 20 wt. % PdAu/C materials in 0.1 mol L⁻¹ NaOH + 10 mM glucose at 20 mV s⁻¹.

Conclusion

Carbon supported Pd-based anode catalysts synthesized from “Bromide Anion Exchange” are active towards the oxidation of various organic multi-carbon compounds. Compared to the Pd/C electrodes, the Ni, Ag and Au contents in the bimetallic materials promote the reactivity of the molecules evidenced by the onset potential shifted towards lower values and the increase in the current densities.

Acknowledgments

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