

Performances of Noble Metal Nanoclusters in the Gas Phase Room Temperature Electrocatalytic Reduction of CO₂ to Hydrocarbons

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Introduction

Recently, there is an increasing interest on the investigation of the characteristics and catalytic reactivity of metal nanoclusters, but limited studies have been made on their properties in gas phase electrocatalytic reactions, notwithstanding the great interest in relation to the development of improved catalysts for fuel cells and other electrocatalytic reactions. One of these interesting other applications is the room temperature electrocatalytic reduction of CO₂ to hydrocarbons. This reaction represents one side of the so called PEC (photoelectrocatalytic) reactor [1-3]. In a PEC reactor, one side is composed of a titania-based photocatalyst which oxidises water to O₂ using solar light. This process produces protons and electrons which are transported to the other side of the device by means of a proton exchange membrane such as Nafion[®] and an electric connection, respectively. On the other side of the PEC reactor protons and electrons react with CO₂ in the presence of an electrocatalyst to produce hydrocarbons and alcohols. The net reaction is thus the conversion at room temperature of CO₂ to fuels/chemicals using solar energy, allowing a net decrease in the emissions of CO₂ into the atmosphere.

One of the critical aspects in this PEC apparatus is the development of the electrocatalyst which should be active at near room temperature, resistant to poisoning, and selective in avoiding side reactions (H₂ and possibly also CO formation). Most of the literature data on the electrocatalytic reduction of CO₂ refer to liquid phase behaviour [4], where the main products are acids such as formic, oxalic and glycolic acids which recovery from aqueous solution is costly. Gas phase electrocatalytic CO₂ reduction is preferable in terms of type of products (Fischer-Tropsch hydrocarbons) and their recovery, but very limited data are available.

The CO₂ electrocatalytic conversion to Fischer-Tropsch type hydrocarbons is a multi-electron transfer reactions. It is expected that multi-electron transfer reactions are favoured by catalysts with high electron density, thus with a high number of surface against bulk metal atoms. In this communication we analyze the characteristics and performances in CO₂ electrocatalytic reduction of Pt and Pd nanoclusters and compare them with those of another class of potentially interesting electrocatalytic materials based on well dispersed Au nanoparticles deposited on base metal oxides.

Experimental

Pt and Pd nanoclusters with mean diameter of around 2 nm were prepared by metal salts reduction (H₂ or LiBH₄ in THF) in the presence of suitable ligands or surfactants (bathophenanthroline sulfonic acid, didecyldimethylammonium bromide) which stabilize the nanoparticles. The deposition-precipitation preparation method was instead used for synthesis of Au nanoparticles (mean diameter around 2-3 nm) supported on Fe₂O₃. For the final preparation of the electrocatalyst, pieces of E-TEK ELAT carbon cloth/GDM (gas diffusion membrane) were coated with a Nafion[®] SE-5112 suspension of the noble metal-based catalyst and then hot pressed with Nafion[®] N-112. Samples were characterized by SEM, TEM and XRD analysis.

Electrocatalytic tests were made galvanostatically at room temperature in a two cell reac-

tor apparatus. Electrode potential was approximately -2 V vs. Ag/AgCl and the current density 20 mA/cm². Analysis of the products was made using GC-TCD and GC-MS.

Results

Characterization of the metal particles was made by transmission electron microscopy (TEM), scanning electron microscopy (SEM), and X-ray diffraction analysis. A narrow distribution of the metal particles size centered at 2-3 nm in all the samples was obtained. The inset of Figure 1 reports a TEM micrograph of Pd nanoclusters which evidences the preparation of round-shaped particles with a relatively narrow distribution of sizes.

Electrocatalytic tests in the gas phase reduction of CO₂ were made at room temperature, using a 1 cm² electrode (amount of catalyst around 1 mg), a constant bias of -1.9922V, and a static closed cell containing 50% CO₂ at near atmospheric pressure. The reaction products detected in the gas phase increased with increasing time of bias application up to a maximum of about 30 min, and then later decreased due to the formation of heavier products which remained adsorbed on the GDM.

The electrocatalytic CO₂ reduction tests showed that the product distribution is influenced by the nature of the noble metal. The product distribution after 30 min (Figure 1) was mainly centred on C1-C2 hydrocarbons and alcohols for Pt nanoclusters, on methanol and also higher hydrocarbons for Pd nanoclusters, and ethane without alcohols formation for gold based electrocatalysts. Pd nanoclusters showed the largest productivity. For longer times the product distribution changes differently depending on the noble metal, due to the formation of heavier hydrocarbons as well as due to CO chemisorption which inhibits reactivity.

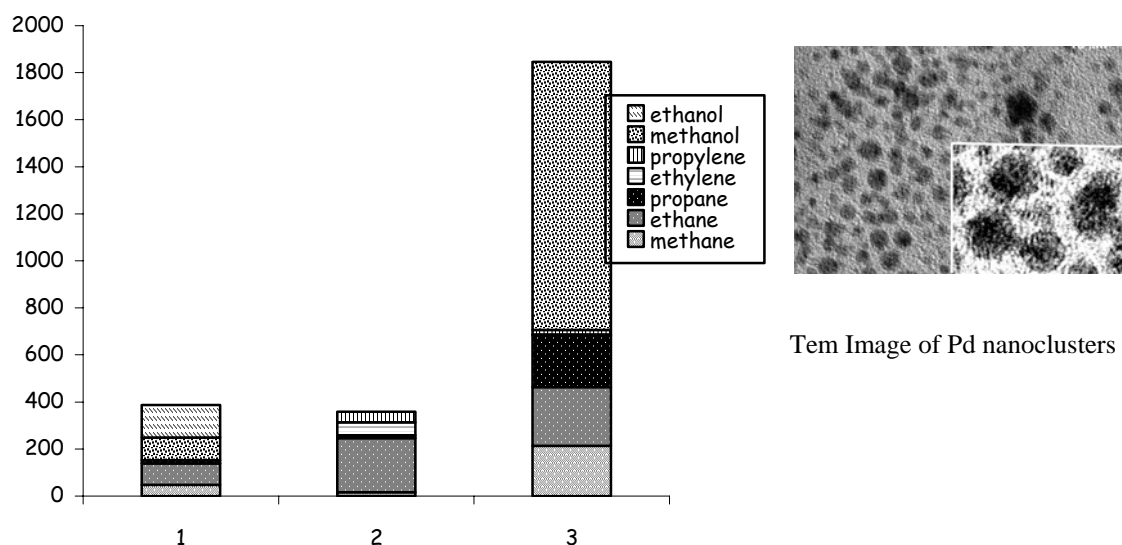


Fig.1 Products (ppm/100cm² electrode) for different electrocatalysts, after a reaction time of 30 minutes: 1) GDM/Pt nanoclusters/Nafion[®]; 2) GDM/Au on Fe₂O₃/ Nafion[®]; 3) GDM/Pd nanoclusters/Nafion[®]

When Pt and Pd nanoclusters performances are compared with those of samples having the same composition, but larger metal particles, a higher activity as well a change in the selectivity is observed. Gold nanoparticles supported on Fe₂O₃ show a reduced sensitivity to deactivation by CO chemisorption with respect to Pt or Pd.

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References

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