

**9th International Symposium on New Materials and Nano-Materials for
Electrochemical Systems
XII International Congress of the Mexican Hydrogen Society
Merida, Mexico, 2012**

**Electron Microscopy and Electrochemical Characterization of Pt/C and Pt-Au/C Catalysts
Synthesized by Surface Redox Reactions**

P. del Angel^{1,*}, R. G. González-Huerta², M. L. Hernández-Pichardo³,
E. Palacios-González¹, J. A. Montoya¹, J. Lara-Peralta²

¹Instituto Mexicano del Petróleo, Dirección de Investigación y Posgrado, Eje Central L. Cárdenas 152, 07730, México, D. F.

²Instituto Politécnico Nacional-ESIQIE, Laboratorio de Electrocatalisis, UPALM, 07738 D.F. México, D.F.

³Instituto Politécnico Nacional-ESIQIE, Laboratorio de Investigación de Físicoquímica y Materiales, UPALM, 07738 México, D.F.

*Tel (5255)9175-8405, pangel@imp.mx

ABSTRACT

Pt-M/C systems (M= metal from groups VIII or IB) are potential electrocatalysts for the fuel cells technology. This work aims to study the oxygen reduction reaction over Pt-Au/C catalysts. The preparation of the monometallic Pt/C catalysts was carried out by means of the impregnation of platinum over graphite. The bimetallic catalyst Pt-Au/C was prepared by selectively depositing Au on supported monometallic Pt/C catalysts by means of the reduction “in-situ” of AuCl_4^- . Redox method used was the Refilling method, which consisted in adsorbing hydrogen first on the metal (Pt), and subsequently reducing the AuCl_4^- species by contact with the Pt-H interface at low temperature. The catalysts were characterized by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM), whereas for the electrochemical tests the catalysts were supported on Vulcan XC-72 carbon and they were evaluated by linear and cyclic voltammetry. The composition of the individual metal particles of the solids indicated the presence of both metals, Pt and Au. A partial Au coating of certain Pt facets is possible, which indicates that the coating mechanism is selective and could influence the catalytic properties of the bimetallic Pt-Au/C catalysts. The electrochemical characterization showed a Tafel slope of -94 mV dec^{-1} for the Pt-Au/C sample, with a 0.62 transfer coefficient, that means a catalytic activity towards the Oxygen Reduction Reaction (ORR).



**9th International Symposium on New Materials and Nano-Materials for
Electrochemical Systems
XII International Congress of the Mexican Hydrogen Society
Merida, Mexico, 2012**

1. Introduction

During the past decades much effort has been done in the study of mono and multimetallic supported catalysts used in the oil refining industry, and electrocatalysts for the fuel cells technology. A fundamental issue on bimetallic catalysts is the interaction between both metals that is not always achieved during the synthesis, but the formation of undesirable non-homogeneous bimetallic aggregates might occur [1], which produces deleterious effects on the catalytic properties of those bimetallic systems. In that case, compositional and structural variations might occur, for example the crystal overgrowths of one metal phase over another, multiple twinning or asymmetric metals aggregation [2]. Indeed, these structural variations may provoke important effects on the activity and selectivity of the supported bimetallic catalysts.

This situation has motivated the search of alternative methods that could offer better control of the metals interaction. Surface redox reactions [3-12] have a great potential for controlling the deposit and location of the second metal over specific crystallographic faces of metal particles [11-12]. For example, graphite supported Pt-Au catalysts [13-14] have been synthesized by surface redox reactions using AuCl_4^- precursors in aqueous solutions, which are reduced by the Pt phase itself or by pre-adsorbed hydrogen acting as reducing agents. The present work explores the use of short-chain low alcohols, for substituting aqueous solutions in the surface redox reactions, i.e. Refilling (RE) method, which was used for selectively depositing a second metal (Au) onto specific crystallographic faces of graphite supported Pt particles on the Pt/C systems. The control of the metal deposits at the nanometric scale could lead to significant applications in catalytic technologies such as fuel cells, fine chemicals production and carbon monoxide oxidation [15-17]. The aggregation state of Pt and Au in the Pt-Au/C bimetallic catalysts synthesized by RE method has been studied at the single particle level and the influence of short-chain solvents was evaluated. Some advanced techniques were used for characterizing the compositional and structural features at the single particle level, such as X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), High Resolution Electron Microscopy (HREM) was studied.

2. Experimental

A monometallic 5 wt % Pt/C catalyst (MC) was used as the basis for synthesizing bimetallic catalysts by surface redox reactions (RE). The monometallic solid was prepared by impregnating a graphite support LONZA LT10 with hexachloroplatinic acid (i.e., H_2PtCl_6 , Aldrich 99.9 %) in absolute ethanol (Merck 99.9 %). After drying at 70°C and reducing the solids at 300°C under H_2 , the presence of small Pt particles having typical diameters between 1 and 10 nm was verified by electron microscopy techniques. These particles spread out on the top surface and edges of the graphite layer stacks, which in turn have a particle distribution between 2 and 20 μm . The metal Pt concentration of the monometallic solids was determined by atomic absorption spectroscopy (AAS), leading to 4.3 % wt. Pt^0 (i.e., MC in Table 1). The metal (Pt) dispersion was determined by H_2 adsorption techniques, which indicated the metal dispersion of the Pt/C catalysts being about 8 %.



**9th International Symposium on New Materials and Nano-Materials for
Electrochemical Systems
XII International Congress of the Mexican Hydrogen Society
Merida, Mexico, 2012**

The parent catalyst Pt/C (MC) described above was modified by adding a second metal close to the electrochemical series of Pt, i.e., Au. The “Refilling” method (RE) was used, which consisted of using a reducing agent like hydrogen, which was pre-adsorbed on the metallic surface (Pt) of the parent catalyst (13). In the present case C_2H_5OH was used as the solvent media. Therefore, Table 1 summarizes the preparation conditions used as well as the compositional data determined by atomic absorption spectroscopy. Also, Table 1 shows the chemical composition data of bimetallic Pt-Au catalysts. The solid RE-70 was obtained by deposition of the second metal (Au) followed by drying at 70°C, without any further treatment.

Table 1. Metal concentration of the catalysts Pt/C and Pt-Au/C (Atomic Absorption Spectroscopy, AAS).

Catalyst	Pt wt %	Au wt %	Preparation conditions (H ₂)
MC	4.3%	-	300°C, 3h
RE-70	4.4%	0.42%	drying at 70°C

The X-ray diffraction (XRD) patterns were obtained in a Siemens D-500 diffractometer fitted with a Cu tube (35 kV, 25 mA) and a graphite monochromator, for eliminating the K β lines. The Au⁰ and Pt⁰ phases were identified after the JCPDS database.

The samples were performed using a Scanning Electron Microscope (SEM) Nova-200 Dual-Beam with Schottky type field emission gun and a resolution of 1.1 nm. It has coupled an energy dispersive spectrometer (EDS) from EDAX, to detect elements from the beryllium onwards. The samples were fixed onto a sample holder using carbon tape. SEM images and EDS were obtained in order to determine the morphology of the nanoparticles and their composition. Furthermore, the samples were studied by high-resolution transmission electron microscopy (HRTEM), the micrographs were obtained in a TITAN 80-300 with Schottky type field emission gun operating at 300 kV. The point resolution and the information limit were better than 0.085 nm. HRTEM digital images were obtained using a CCD camera and Digital Micrograph Software from GATAN. The elemental composition was determined by Energy dispersive X-ray spectroscopy (EDS) with an EDAX spectrometer fitted to the TEM. In order to prepare the materials for observation, the powder samples were ultrasonically dispersed in ethanol and supported on holey carbon coated copper grids.

A conventional single three-electrode test electrochemical cell was used in the electrochemical experiments. All of the electrode potentials in this work are related to a normal hydrogen electrode (NHE) in a 0.5 M H₂SO₄ aqueous solution electrolyte. The electrochemical measurements were performed using a Potentiostat AUTOLAB. All electrochemical experiments were conducted at room temperature. The working electrode was a glassy carbon disk with a 5 mm diameter (0.19 cm²). Glassy carbon and reference hydrogen electrodes were used as the counter and the reference electrode. The catalytic ink was prepared by dispersing 1 mg of catalyst in 8 μ L of Nafion® and 60 μ L of

ethyl alcohol in an ultrasound bath for 15 min. A drop containing 8 μL of catalyst ink was deposited onto the working electrode surface and dried at atmospheric conditions. The electrodes were activated in an oxygen free electrolyte, by scanning the potential in a region between 1.2V/NHE to 0.0 V/NHE at 50 mV /s for 10 cycles, until a steady state voltamperogram was reached. Thereafter, the electrolyte was saturated with pure oxygen for 30 min and maintained on the electrolyte surface during rotating disk electrode (RDE) experiments. Hydrodynamic experiments were recorded in the range of rotation rate of 100 to 1600 rpm at 5 mV/s.

3. Results and discussion

The X-ray diffraction patterns corresponding to the Pt/C (MC) and Pt-Au/C (RE-70) bimetallic catalysts prepared by RE method are reported in Figure 1. The vertical line around 38.18° (2θ) indicates the theoretical position of the Au(111) peak. For the bimetallic catalyst, RE-70, the XRD peaks do not change of position, this means that Au^0 and Pt^0 is not an alloy.

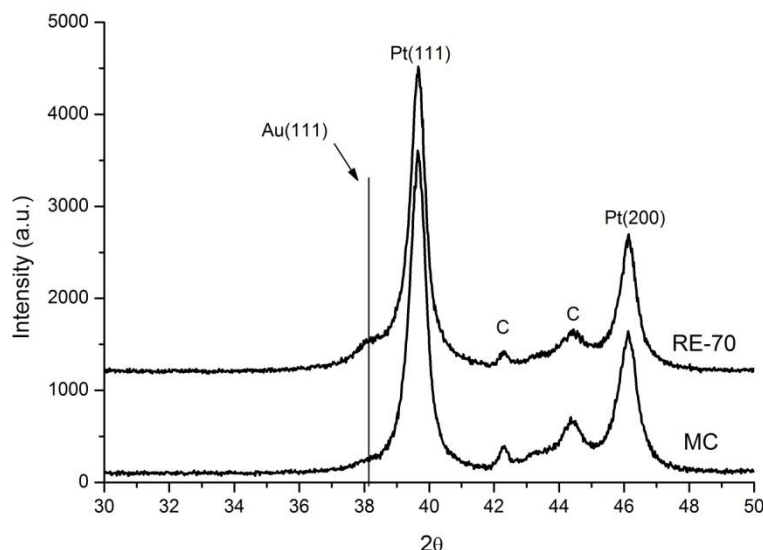


Figure 1. XRD patterns of the monometallic Pt/C (MC) and bimetallic Pt-Au/C (RE-70) catalysts.

Table 2 shows a comparison between the mean particle diameters determined by X-ray diffraction and TEM. The difference might be due to overestimation of the crystallite diameters by XRD arising from instrumental artifacts [18-19].

**9th International Symposium on New Materials and Nano-Materials for
Electrochemical Systems
XII International Congress of the Mexican Hydrogen Society
Merida, Mexico, 2012**

Table 2. Mean particle diameters determined by TEM and XRD.

Catalyst	MET Ds (Å)	XRD	
		Dv Pt (Å)	Dv Au (Å)
MC	110	140	--
RE-70	100	170	70

SEM image and EDS of RE-70 bimetallic catalyst are shown in Figure 2. White spots correspond to Pt-Au bimetallic nanoparticles, the corresponding EDS was obtained from all the region of the SEM image (global analysis). The quantification of gold and platinum is a little lower compared with the AAS analysis.

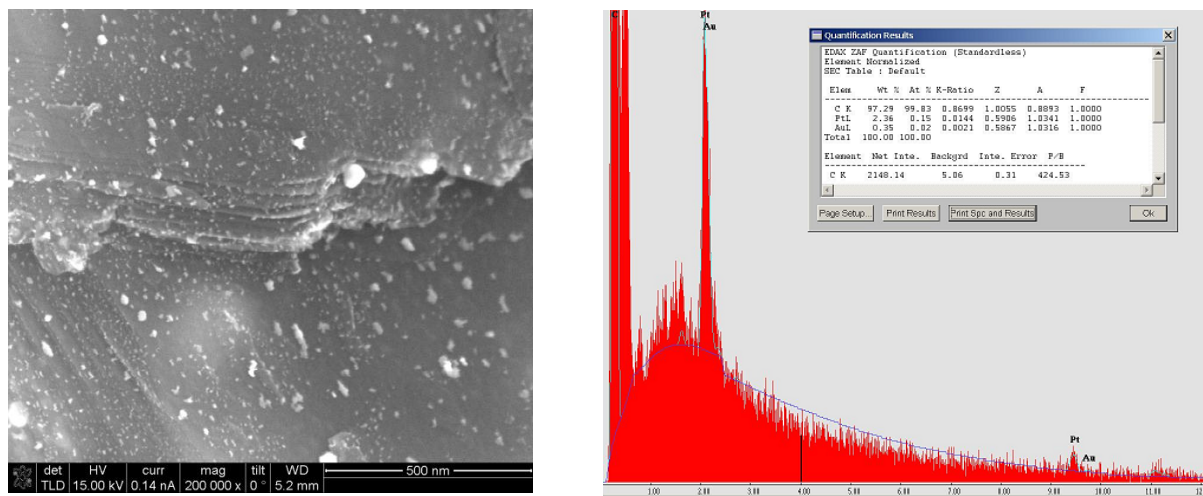


Figure 2. SEM image and EDS analysis of Pt-Au/graphite bimetallic catalyst.

The chemical composition of the single metal particles was determined by Energy Dispersive Spectroscopy (EDS) in a TEM in two modes. The first consisted of using a narrow electron beam probe ($\phi \sim 1 - 2$ nm) for microanalysis of single particles, while the second mode was performed using large beam probe diameters, i.e., 1 to 10 μm , for the global analysis of sample regions containing hundreds of metal particles to obtain the average composition. As expected, the global analyses indicated a concentration of Pt higher than Au (similar to the EDS obtained by SEM), while the point analyses indicate a mixed situation, where single particles may be either richer in Au or Pt. Although particles containing only Au were not found, about 5 % of the particles analyzed contained only Pt, thus indicating a close contact of the Au phase with the Pt phase at the nanometric scale. These results might be explained

considering the formation of a layer of Au on top of the metal particles, which is detected only by EDS methods, because the conventional chemical analysis (AAS) gives only “bulk composition”, without taking account of the metal phase distribution.

The interaction between both metals at the single-particle level was studied by direct lattice resolution imaging, using high resolution electron microscopy techniques. Thus, Figure 3 displays the lattice image of a metal particle after the deposit of the second metal (Au). Here, one observes a metal particle consisting of two parts, one located in the center of the particle with a lattice spacing of about 0.22 nm, while the other located outer of the particle with a lattice spacing of about 0.235 nm. This was confirmed by the EDS obtained from this single Pt-Au nanoparticle.

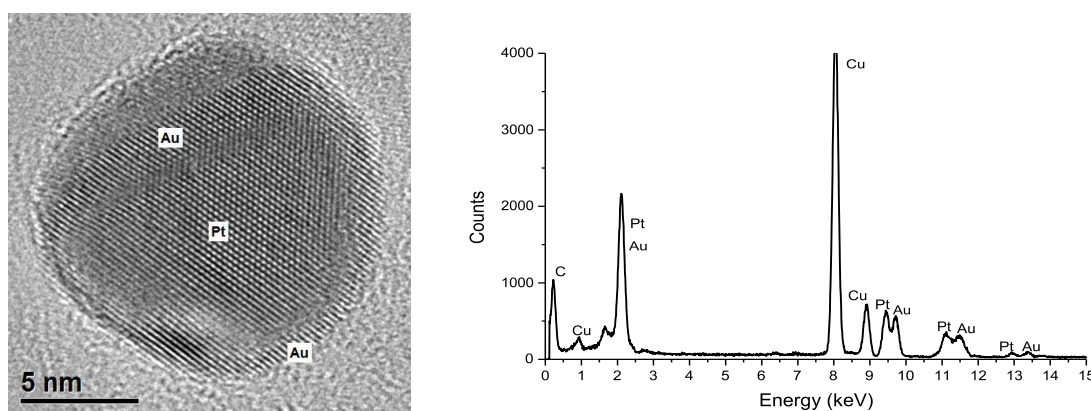


Figure 3. HRTEM and EDS analysis of a single Pt-Au nanoparticle on the RE-70 bimetallic catalyst.

Figure 4 shows RDE experiments. The polarization curves on Pt-Au/C, incorporated into a Nafion® film electrode, were performed at different rotation rates, in an oxygen-saturated 0.5M H₂SO₄ solution at 25°C. The polarization curves show three well defined potential zones: charge transfer, mixed and mass transport. It was considered that defined limiting currents are associated with the high diffusion of oxygen through the electrode surface and the uniform distribution of active sites. A similar polarization curve was observed on the Pt/C electrode. In these electrocatalysts, the oxygen reduction is fast enough that, at high overpotentials, a flat limiting plateau is observed. This phenomenon can be associated to a good distribution of the electrocatalytic sites on the electrode surfaces. On a film-coated electrode surface, the overall measured density current (j), is related to the kinetic density current (j_k) and the boundary layer diffusion-limited current density (j_L). Thus, the overall measured current of the oxygen reduction can be written as being dependent on the kinetic current and the diffusion-limited current, as shown on the left side of the equation 1.

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_L} = \frac{1}{j_k} + \frac{1}{B\omega^{1/2}}, \quad (1)$$

The kinetic current density is proportional to the intrinsic activity of the catalyst, and the diffusion-limited current density is proportional to electrode rotation rate (ω). The constant B is $0.2nFCD^{2/3}\nu^{-1/6}$, where 0.2 is a constant used when ω is expressed in revolutions per minute, C is the bulk concentration of oxygen ($1.1 \times 10^{-6} \text{ mol cm}^{-3}$), D is the diffusion coefficient of oxygen in the sulfuric acid solution ($1.4 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), and ν is the kinematic viscosity of the sulfuric acid ($1.0 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$).

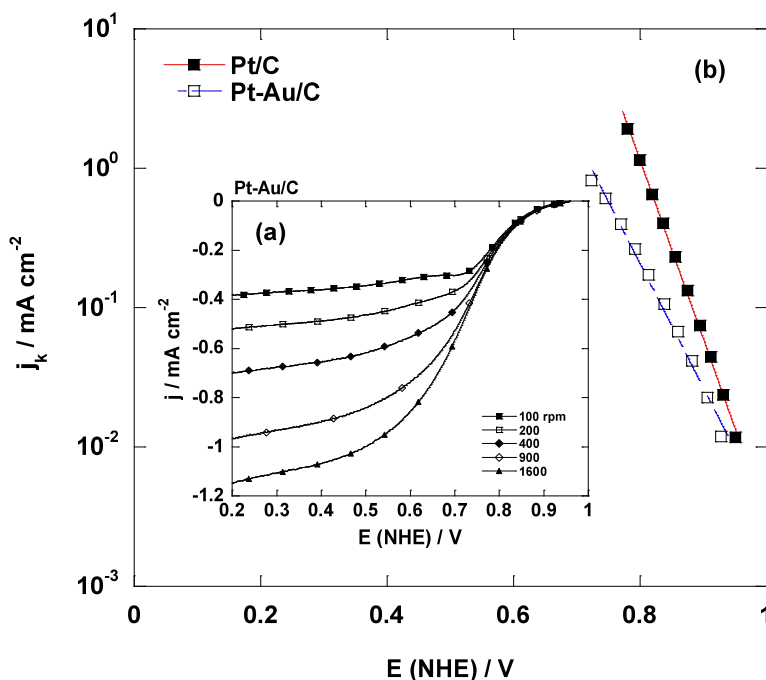


Figure 4. RDE responses on supporting Pt/C and Pt-Au/C electrodes in O₂ saturated 0.5 M H₂SO₄: a) Linear Voltammetry, b) Tafel plots.

The Figure 4(b) shows the mass-transfer-corrected Tafel plots for the Pt/C and Pt-Au/C electro-catalysts. Tafel slopes at low current density have a value of 80 mV dec⁻¹ and 94 mV dec⁻¹ in the Pt/C and Pt-Au/C respectively, which indicate that the first electron transfer on the adsorbed oxygen molecule is the rate-determining step. This behavior is in agreement with results reported by other authors for Pt/C and Pt-Au/C catalysts prepared by other methods [20-21].

4. Conclusions

**9th International Symposium on New Materials and Nano-Materials for
Electrochemical Systems
XII International Congress of the Mexican Hydrogen Society
Merida, Mexico, 2012**

The application of surface redox methods using alcohol led to the reduction “in-situ” of AuCl_4^- species and the selective deposit of Au^0 onto the (111) faces of Pt small particles. At room temperature most of the small metal particles analyzed showed the presence of both metals, Pt and Au. The aggregation state of the small metal particles was sensitive to the preparation method. Also, the preferential decoration of Pt(111) particle facets with Au was verified by high resolution electron microscopy techniques.

The electrochemical characterization showed a Tafel slope of -94 mV dec^{-1} for the Pt-Au/C, which indicates that the first electron transfer on the adsorbed oxygen molecule is the rate-determining step. The Pt-Au/C catalyst shows catalytic activity towards the Oxygen Reduction Reaction (ORR).

5. Acknowledgements

The authors thank the facilities of the Electron Microscopy Laboratory of the Instituto Mexicano del Petróleo. This work has been supported by the IPN project SIP- 20120486, SIP-20120475, multidisciplinary project IPN-SIP 1338 and project ICYTDF PIEMP11-31.

6. References

- [1] Nagy, J. B., Barette, D., Fonseca, A., Jeunieu, L., Monnoyer, Ph., Piedrigross, P., Ravet-Bodart, I., Verfuillie, J. P., and Wathélet, A., In Nanoparticles in Solids and Solutions; J.H. Fendler and I.Dékány, Eds.; Kluwer Academic Publishers: Dordrecht, 18, 71, (1996)
- [2] Chandler, B.D., Schabel, A. B., and Pignolet, L. H., J. Phys. Chem. B 105, 149 (2001)
- [3] Barbier, J., Advances in Catalyst Preparation, Study Number 4191 CP, Catalytica Studies Division. Mountain View, (1992)
- [4] Menezo, J. C., Denanot, M. F., Peyrovi, S., and Barbier, J., Appl. Catal. 15, 353 (1985)
- [5] Barbier, J., Menezo, J. C., Montassier, C., Naja, J., Del Angel, G., and Domínguez, J. M., Catal. Lett. 14, 37 (1992)
- [6] Barbier, J., Boitiaux, J. P., Chaumette, P., Leporq, S., Menezo, J.C., and Montassier, C., Eur. Patent 380 402, assigned to Institut Français du Pétrole, (1990)
- [7] Marecot, P., Barbier, J., Mabilon, G., Durand D., and Prigent, M. Eur. Patent 92 90516-2, assigned to Institut Français du Pétrole, (1992)
- [8] Dumas, J. M., Geron, C., Hadrane, H., Marecot, P., and Barbier, J., J. Mol. Catal. 77, 87 (1992)
- [9] Menezo, J. C., Hoang, L. C., Montassier, C., and Barbier, J. React. Kinet. Catal. Lett. 46 (1), 1 (1992)
- [10] Barbier, J., Dumas, J. M., Geron, C., and Hadrane, H., Appl. Catal. 1990, 67, L1.
- [11] Barbier, J., Marécot, P., Del Angel, G., Bosch, P., Boitiaux, J. P., Didillon, B., Dominguez, J. M., Schifter, I., and Espinosa, G., Appl. Catal. A: Gral. 1994, 116, 179.
- [12] Espinosa G, Del Angel G, Barbier J, Bosch P, Lara V, and Acosta D, J. Mol. Cat. A: Chem., 164, 253 (2000).



**9th International Symposium on New Materials and Nano-Materials for
Electrochemical Systems
XII International Congress of the Mexican Hydrogen Society
Merida, Mexico, 2012**

- [13] Del Angel, P., Dominguez, J. M., Del Angel, G., Montoya, J. A., Lamy-Pitara, E., Labruquere, S., and Barbier, J., *Langmuir*, 16, 7210 (2000).
- [14] Del Angel, P., Domínguez, J. M., Del Angel, G., Montoya, J. A., Capilla, J., Lamy-Pitara, E., and Barbier, J., *Topics in Catalysis*, 18, 183 (2002).
- [15] Haruta, M., Yamada, N., Kobayashi, T., and Iijima, S., *J. Catal.*, 115, 301 (1989).
- [16] Haruta, M., Tsubota, S., Kobayashi, T., Kageyama, H., Genet, M. J., and Delmon, B., *J. Catal.* 144, 175 (1993).
- [17] Haruta, M., *Catal. Today*, 36, 153. L. Vegard, *Z. Phys.* 5, 17 (1997)
- [18] Thorpe, M. F., and Garboczi, E. J., *Phys. Rev. B* 42, 8405-8417 (1990).
- [19] Domínguez, J. M., Simmons, G. W., and Klier, K., *J. Molec. Catal.* 20, 369 (1983).
- [20] B. Ruiz Camacho, M. Torres Rodríguez and O. Solorza-Feria, *J. New Mat. Electrochem. Systems* 12, 043-047 (2009).
- [21] G. Vázquez-Huerta, G. Ramos-Sánchez, A. Rodríguez-Castellanos, D. Meza-Calderón, R. Antaño-López, O. Solorza-Feria, *Journal of Electroanalytical Chemistry* 645, 35–40 (2010)