FACTORES QUE AFECTAN LA ACTIVIDAD DE UN CENTRO CATALÍTICO

ON THE FACTORS AFFECTING THE ACTIVITY OF A CATALYTIC CENTER

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The author dedicates this work to the commemoration of the 50th anniversary of the Electrochemistry Laboratory of the Faculty of Sciences of the Universidad de Los Andes (ULA).

Resumen

En este trabajo se discute un marco de interpretación experimental del desplazamiento electrónico de un sitio catalítico. Aunque esta interpretación no es nueva, se cree que es importante presentar este contexto mencionando los ejemplos obtenidos hasta ahora en dos soportes diferentes, como son, el carbono grafítico y los óxidos semiconductores. Los cambios en la propiedad electrónica de los sitios catalíticos tienen el efecto de modificar la energía de adsorción de la especie reactiva, como se discute utilizando el monóxido de carbono como sonda molecular.

Palabras clave: Sitios catalíticos, Interacción con el soporte; Interfaz; Electrocatálisis; Propiedades electrónicas.

Abstract

In this paper, a framework of experimental interpretation of the electronic shift of a catalytic site is discussed. Although this interpretation is not new, we believe it is important to present this context by mentioning examples obtained so far on two different supports, namely, graphitic carbon and semiconductor oxides. Changes in the electronic property of the catalytic sites have the effect of modifying the adsorption energy of the reactive species, as discussed using the carbon monoxide as a molecular probe.

Key words: Catalytic sites, Support Interaction; Interface; Electrocatalysis; Electronic properties.

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1. Introduction

The catalytic material supports may be of an electronic or non-electronic conductive nature. Their use in supporting nanoparticulate materials, in catalysis and electrocatalysis, is very common. The role played by the support was until recently not considered to be important as it was thought to be an inactive material necessary for the dispersion of the active phases and providing a pathway for electron charge transport. It was considered that its presence could generate additional difficulties for the proper functioning of the shaped electrode material, such as, the lack of chemical stability in the electrolytic medium; the increase in volume; and an additional mass of non-active material decreasing the specific energy. However, the altered chemisorption property of some reduced noble metals observed on the surface of titanium oxide reported by Tauster et al.,[1-3] put in evidence the strong interaction support with the catalytic sites, and led to coin such an effect as “strong-metal-support-interaction (SMSI)”. One has to state that metal support interaction has been known in catalysis since the second half of the 1960s as reported by Schwab and Derleth[4], and Solymosi[5].

It is clear, that this phenomenon provides an extra variable for the optimization of the catalytic sites and paved the way to the observation of such a phenomenon in electrocatalysis[6-10] relevant to energy converting devices that involve, e.g., the hydrogen reactions (HER/HOR); the oxygen reactions (ORR/OER). In this short essay, we discuss what is meant by the special role played by the supports, and its implication in modifying the electronic properties of a catalytic center as a result of the interaction with the support, and the simple way to detect it by means of surface electrochemistry.

2. Graphitization versus oxides domains

2.1. Graphitic sites

In low temperature fuel cells, e.g., the most popular support is amorphous carbon. There is a wide variety of geometrically and chemically complex supports with different geometries, sizes and porosity allotropes. These characteristics can influence, in different ways, the electrocatalytic centers. The most desirable properties are taken into account when considering a theoretical modeling of the system. One of these properties is that the support has a high electronic conductivity, a property necessary for electrocatalytic systems (contribution to the reduction of the ohmic drop). Therefore, the interaction of metal nanoparticles with the support, for example, on graphitic domains is of great importance.

The reasons that give rise to this effect deserve a proper analysis. That is why the study of graphitic domains (sp^2 versus sp^3) is driven on supports such as carbon black (e.g., XC-72), graphene oxide (rGO), multiwall carbon nanotubes (MW-CNTs), nanofibers (NFs) and even on MXenes[11], since these materials used as supports show interesting electrochemical characteristics for various electrochemical reactions of technological interest. Herein, the proper technique to titrate graphitic (G) versus defect (D) carbon domains, is the Raman spectroscopy. For carbon-based materials, two important Raman lines belonging to D, and G bands, in the wavenumber interval between 1100 cm^{-1} and 1800 cm^{-1}, show the high degree of disorder. This technique also facilitates the detection of C-C defects and therefore discloses on the synthesis quality of carbon-based materials. The analysis of the Intensity I_D/I_G ratio allows the knowledge of the defects/sp^2 contribution, on the one hand, and on the other hand, to quantify the in-plane crystallite size, L_a[12], variation in the carbon material, that can be determined via the equation: $L_a(nm)=2.4\times10^{-10}\ \lambda^4_{laser} I_G/I_D$.

A nice correlation of La with the chemical stability of the catalytic center (Pt) was experimentally demonstrated[13]. This was successfully done by direct nucleation using the selective photo-deposition technique[14] of metal nanoparticles on the sp^2 domains of carbon. Here, it is important to point out that a chemical reduction for the deposition of metal nanoparticles is not selective, because the nucleation of metal nanoparticles take place indistinctly at any carbon site (C-C defects; sp^2, sp^3, etc.,). A simple method of detection, in surface electrochemistry, of the change of the adsorption energy of the catalytic center due to an electronic change of the material by the SMSI effect, is the molecular probe through the electrochemical CO stripping[15-17]. The global electrochemical oxidation, in acid, of carbon monoxide can be written as follows:

$$CO + H_2O \longrightarrow CO_2 + 2H^+ + 2e^-$$

Moreover, this reaction can be thought as a set of two steps:

$$CO_{ads} + OH_{ads} \longrightarrow CO_2 + H^+ + e^-$$

Herein, OH_{ads} indicates a partial oxidation of the metal:

$$M + H_2O \longrightarrow M\text{-}OH_{ads} + H^+ + e^-$$

One recalls that on platinum electrode surface the adsorption of CO is accompanied by the backdonation of d-orbital of platinum in the 2π* antibonding orbital of CO, a phenomenon known as the Blyholder-Bagus back donation mechanism[18,19].

As illustrated in Figure 1 (panel (b)), the oxidation of adsorbed CO on platinum sets on at 0.69 V/RHE, and peaks, as it is well-known, at 0.77 V/RHE on Pt/Vulcan XC-72. On Pt/HOPG (Highly Oriented Pyrolytic Graphite), this process is shifted to lower applied electrode potential by ΔE = - 90 mV.

Indeed, on a platinum surface with a higher electron density this process of oxidation sets on at 0.6 V/RHE and peaks at 0.68 V/RHE. This significant shift for a one-metal center catalyst highlights indistinctly the role of the nature of the support, i.e., the graphitic domains sp^2. It is important to emphasize that regardless of the concentration of the sp^2 domains, the photons can selectively favor the metal atoms nucleation at sp^2 domains. In addition, the charge of the Pt atoms on top modifies the charge donated to the CO molecule was revealed by XPS analysis[15], see in Figure 1 (panel (a)). This phenomenon, just displayed in figure 1, was experimentally sustained in an earlier publication[13, 15].

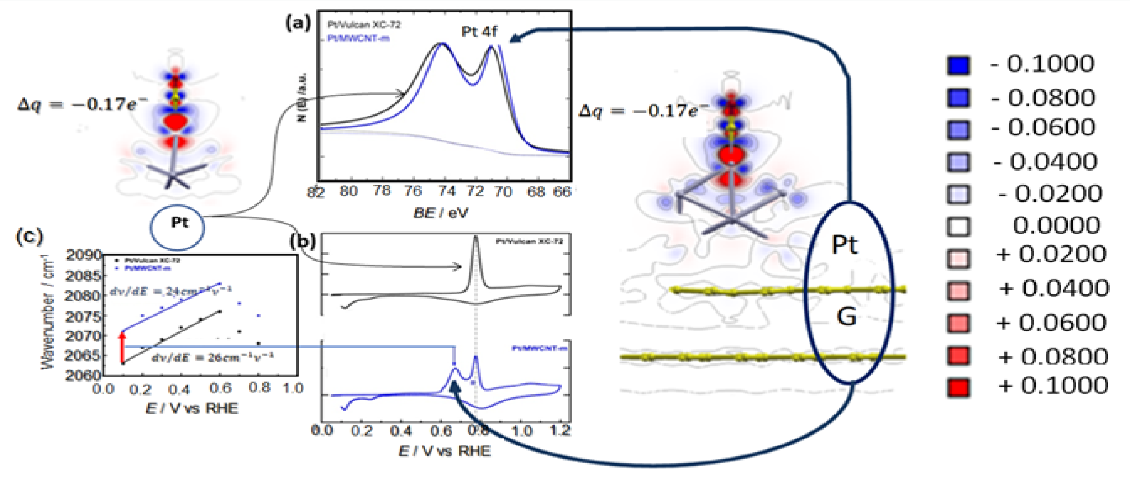

Figure 1. CO stripping, in 0.5 M H_2SO_4 on Pt (NPs) chemically deposited on amorphous carbon; multi-wall carbon nanotubes, MW-CNT, (panel b). The effect of the SMSI effect is observed in the Pt 4f emission line shift toward lower binding-energy (panel a). The Bader charge distribution, deduced by DFT, is indicated in the left and right side of the figure comparing the atoms on sp^3 versus those in sp^2 hybridization. Insert in panel b shows the Stark effect in FTIR measurements. The Stark effect in FTIR measurements is shown in panel c.

The only difference lies in the extension of these sp^2 domains in relation to the increase in the corrosion resistance and/or agglomeration of the nanoparticles when subjected to anodic corrosion potentials (>1.2 V/RHE) of the nanoparticulated metal and/or graphitic centers.

In brief, the interaction of nanoparticles with the support is manifested by changes in the electronic structure of the nanoparticles. These are reflected in electrocatalytic reactions[20-26]. Through the electrochemical oxidation of CO (stripping process), such changes can be associated with a different

CO adsorption energy as a result of the interaction with the support. Moreover, one has to recognize that the interaction effect of two dissimilar materials is rather complex, in the sense that, different adsorption sites affect the adsorption energy of CO, since the carbon monoxide molecule, adsorbing very close to the support-nanoparticle interface, does not have a positive effect, but induces a negative one, leading to the separation of the nanoparticle from the support[27]. On the other hand, defects, for instance, vacancies are very reactive, and lead to earlier oxidation of the support to produce CO_2 [28, 29].

The use of dopants atoms in graphene, like N sounds an advantage since the interaction energy increases and the probability of support oxidation decreases at anodic electrode potentials, e.g., in the fuel cell system, in the cathodic reduction of molecular oxygen. Though, the presence of nitrogen-doped sites is then important to keep the metallic cluster attached to the support[30]. Moreover, the use of computational methods, is also possible to screen various modifications that are expected to have exponential growth leading to the discovery of more active and stable electrocatalysts.

2.2. Oxide sites

As mentioned in the introduction, the importance of the chemical nature of the supports on the carrier effect was mainly demonstrated by many catalytic investigations on metals supported on oxide materials. It is clear that semiconductor oxides, which can modulate the interaction with the support and charge transfer characteristics are based on the physics of semiconductors. An electronic interaction, indeed, develops as a result of the different Fermi levels of each phase, e.g., between a metal/semiconductor interface. This is due to the Schottky theory of metal-semiconductor contact in thermodynamic equilibrium. At this point, the flow of electrons develops a region of positive space charge in the semiconducting oxide. Concomitant to this, experimental data reported by e.g., Tauster et al.,[2, 3] and Solymosi[5], clearly indicated an enhanced catalytic behavior of the supported catalyst. The reason for this phenomenon, as a result of a charge transfer at the metal-oxide interface, is undoubtedly the ligand effect through the d-band interaction between the metallic catalytic site and the metal of the oxide site phase, namely: hybridization. A phenomenon rather similar to that at metal-graphitic sites: i.e., d-sp^2 one, discussed in section 2.1. All of this points to a clear change in the chemical nature at the interface between the metal and oxide sites. In fact, in a previous work the presence of a platinum-tin alloy was revealed by X-ray analysis[10], and latter evaluated by means of a direct chemical synthesis alloy[31]. The Pt-TiO_2 system was examined by DFT revealing Pt–Pt, Pt–O, and Pt–Ti interactions[32], and the covalent bond formation of Pt nanoparticles on doped-Titania (Pt-M:TiO_2/C (M= Y, Ce)) was further assessed[33]. Similar effects were for platinum nanoparticles on other oxides, such as WO_3 [7] and SnO_2 [34]. The CO stripping analysis surface electrochemical features recorded on synthesized Pt_3Sn[35] revealed similar features of Pt photo-deposited onto SnO_2 [34].

Due to the semiconducting nature of most of the metal oxides, a synthesis of these oxides in the presence of carbon was chosen, giving rise to oxide-carbon composite material. Thus, a previous evaluation of the mass loading (0 to 100%) of each component established that the electrical conductivity is maintained up to a mass loading of 50% meeting the requirements for the use of oxides as supports for nanoparticulate catalysts[36]. In this manner, the electronic conductivity of nanoparticulate catalysts supported on pure and/or doped oxide can be guaranteed by the presence of carbon, stimulated by the selective photo-deposition process of, e.g., platinum nanoparticles on the oxide sites, as compared to any chemical deposition synthesis. The SMSI effect was easily visualized in the CO stripping process, and the results regarding the oxidation energy was similar to that recorded on graphite (sp^2 sites). Again, the SMSI effect that produced the oxidation potential shift of adsorbed carbon monoxide monolayer was beneficial to enhance the kinetics of the ORR.

3. Concluding Remarks

In this essay, we try to summarize the important events about the phenomenon that leads to an electronic modification of the catalytic center which is favorable for the electrocatalytic enhancement of a reaction of technological interest. Surface electrochemistry (CO stripping) only detects a change in the electronic property, as well as Fourier transform infrared spectroscopy (FTIR), and XPS. However, we can say that the effect, either on graphitic sites or metal sites of the oxide is the formation of a covalent bond (hybridization) as estimated in the theoretical DFT calculations. On carbon, used as support, its graphitic domains store electrons in the π-π lattice, thus, the support acts as a mediator and stabilizer if coordination bonds are created between the d orbitals of the metal active sites and the π-π lattice. However, on the oxides, we consider that the reactivity to form, at the interface, a chemical bond of the catalytic center with the metal of the oxide, is the strong energy present during the nucleation process when electron-hole is generated during the photo-deposition process.

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