Evaluation of Adsorption Properties of Platinum Catalysts for Proton Exchange Membrane Fuel Cells: Establishing Criteria for the Standardization of Active Area Measurements

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The adsorption properties of the standard commercial ETEK Pt (20 wt %)/Vulcan XC72 catalyst have been evaluated using H_2 and CO as probe molecules. The influence of the surface chemistry of the carbon black support has been observed to play a crucial role on the catalyst behavior. The analysis of the impact of the pretreatment conditions on the determination of the metal surface area calculated on the basis of the specific adsorption of the probe molecules on the surface Pt is thoroughly discussed in order to provide a series of criteria for the catalyst active area measurement in proton exchange membrane fuel cell electrodes.

Introduction

Proton exchange membrane fuel cells are attracting a great deal of attention in the last years as a promising technology for highly efficient energy conversion with low pollutants emission.[1] One of the main drawbacks for their commercialization is the excessive cost of their components resulting from the high Pt content in them.[2] By now, Pt and Pt–Ru alloys dispersed on electrically conductive carbon blacks with metal loadings between 20 and 60 wt % are by far the preferred catalysts for electrodes. Numerous efforts have been devoted to develop high-performance membrane-electrode assemblies with reduced loadings of the precious metal.[3,4] Different approaches to solving this issue are focused in the synthesis of catalysts with smaller particle sizes or the introduction of changes in the catalytic layer design.[5] The modifications in the structure and composition of the catalytic zone to achieve those targets usually consist of adding certain amounts of proton-conducting compounds to improve the proton-transfer process toward the membrane, optimizing the catalytic layer thickness, or synthesizing the catalytic layer directly onto the membrane.

Assessment of literature data on this subject is hindered by the inconsistency of results when comparing the performance of components regarding their active metal surface areas and the Pt utilization degree in them.[6] Take as an example the comparison of surface area values reported for a widely used commercial catalyst, such as the standard Pt(20 wt %)/Vulcan XC72 from E-TEK. Values lower than 30 m^2/g_{Pt},[7–9] between 50 and 90 m^2/g_{Pt},[10–13] or above 100 m^2/g_{Pt} [14–16] can be found for this catalyst in the literature using techniques such as cyclic voltammetry, X-ray diffraction, small-angle X-ray scattering (SAXS), transmission electron microscopy, chemisorption, etc. The ambiguities in the measurements and the disparity of these values have their origin in the concept of surface area.

The real surface area meaning depends on the measurement method, the conditions of the measurement tests, and the theory and assumptions on which the method is based. Thus, for a given system, various “surface areas” could be defined depending on the measurement method, the probe, and the conditions used. From this standpoint, the surface area of Pt in PEM catalysts becomes a relative concept that must be taken into consideration together with other characteristics such as the dispersion of the active metal, the metal particle size, the surface topography, the heterogeneity or the surface, its chemical modification, the presence of functional groups, and the addition of polymers (PTFE, PFSA, etc.), metals, or ions, which can cover the metal, form alloys, or modify the adsorption/absorption properties of the

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systems.[15,17] All these topics are closely interrelated and must be thoroughly taken into consideration for data normalization and correct assessment of the characterization and performance data. Depending on the technique and the conditions used, some properties may contribute to overestimating or undervaluing the exposed metal surface.

Determination of the Pt specific surface area defined as the effective area per unit of Pt mass becomes an essential property to define these systems. The statement of benchmarks for the design and characterization of components in PEM fuel cells demands establishing criteria for the standardization of active area measurements in their catalysts and a thorough knowledge of their adsorption properties.

The study here reported analyses the adsorption properties of the commercial E-TEK Pt (20 wt %)/Vulcan XC 72 standard catalyst, which is widely used for research work in the literature. H_2 and CO have been used as probe molecules for the estimation of the catalyst surface thermally treated under vacuum. The evaluation of its adsorption properties in a medium free from competitive adsorption with other molecules and the impact of the surface chemistry of the carbon black support on the catalyst behavior is the first step for assessing the surface area values obtained by different techniques. It must be considered that the characterization of components such as inks, gas diffusion electrodes, or carbon-catalyzed membranes synthesized from a given catalyst may often hinder some peculiarities of the catalyst itself. The characterization procedure of the catalyst on those components should take into consideration the properties of the catalyst itself as a reference.

Experimental Section

The standard Pt (20 wt %) on Vulcan XC72 catalyst from E-TEK was used for characterization. Additional experiments were carried out on Vulcan XC72 (Cabot Corp.) carbon black as reference for the support.

To determine the minimum desorption temperature of the adsorbed species, which could interfere with the adsorption of probe molecules, and analyze the surface functional groups in the analytes, we submitted the samples to a thermogravimetric test coupled with mass spectrometric analysis. Aliquots of 3–5 mg of sample were heated under a stream of N_2 or N_2/O_2 at a flow rate of 0.6 L h^{-1} applying a linear temperature ramp of 25 K/min. Mass losses in the sample were determined with a Mettler thermobalance, whereas the effluent gas was analyzed with a quadrupole mass spectrometer (Pfeiffer Vacuum Thermostar). The ion currents for several mass-to-charge ratios in the range between 2 and 100 were registered with time.

Chemisorption of probe molecules (H_2 and CO) and temperature-programmed desorption (TPD) experiments were carried out in a conventional glass volumetric system capable of maintaining a vacuum of 1×10^{-6} Torr by means of a turbo pumping system (Varian Turbo V70 LP and SH110). Samples of 30 mg were charged in a glass bulb connected to the volumetric adsorption system. After the air in the bulb was evacuated, the sample was heated at the required temperature under dynamic vacuum and maintained for 2 h under those conditions. The sample was then cooled to 298 K, and the adsorption isotherm was measured. The chemisorbed amount has been calculated by extrapolating the linear part of the isotherm curve to zero equilibrium pressure. After adsorption of probe molecules, the gas phase in the bulb was removed and the sample was maintained under dynamic vacuum for 15 min. A TPD test was then performed by applying a linear temperature ramp of 10 K/min to the sample bulb. The species desorbed from the catalysts were analyzed in a quadrupole mass spectrometer (Quadstar QMS 200 M2) equipped with channeltron and faraday detectors, which is directly attached to the vacuum system. Ion currents for a number of mass-to-charge ratios were collected on an interfaced computer. A new sample of catalyst was used for each adsorption essay. In some cases, after measuring the H_2 adsorption isotherm, the sample was contacted with air to oxidize chemisorbed hydrogen, and a new adsorption cycle was performed by pretreating the sample under dynamic vacuum for 2 h at the same temperature as in the previous cycle. A new H_2 adsorption isotherm at 298 K was then measured.

Additional hydrogen chemisorption measurements were also tried in a pulse-flow apparatus (Micromeritics 2700 Pulse Chemisorb). After the catalyst was submitted to equivalent pretreatments, several pulses of 50 μL of H_2 were then dosed onto the catalyst. The amount of hydrogen not adsorbed in each pulse was determined by a thermal conductivity detector.

X-ray diffraction tests were also performed on the previously heat-treated samples in order to check whether the thermal treatment of the catalyst had had any effect on increasing its particle size.

Results

Temperature-Programmed Tests. To apply a soft treatment to remove adsorbed species from the catalyst before chemisorption measurements and avoid structural changes of the metal particles by thermal sintering, we initially submitted the as-received catalyst to a TPD test. The catalyst was studied thermogravimetrically under an inert flow of gas, which was simultaneously analyzed by mass spectrometry. The obtained thermogravimetric curves for the E-TEK catalyst in Figure 1A indicate two main mass losses. The mass spectrometric analysis of the effluent reveals that the first one is mainly due to water (peak at 350 K) and the second one at 555 K to SO_2 desorption (*m/z* ratios 64, 48, and 66) (Figure 1B). At temperatures above 1000 K, a new SO_2 evolution is observed with a maximum at 1225 K.

To elucidate the origin of the presence of sulfur species in the catalyst, we analyzed a sample of Vulcan XC72 in the same way. Figure 2 presents the results obtained from the thermal analysis of the support. The differential thermogravimetric curve indicates a much lower mass loss at a given temperature in the absence of Pt. SO_2 desorption takes place at 555 K, as previously seen in the catalyst, although its formation at higher temperatures does not occur in this case, at least up to 1273 K. The adsorbed water content in this sample is much lower and not detected in the analysis.

An additional TG-MS test on Vulcan XC72 was performed in the presence of oxygen aiming to determine if all sulfur in the support had been removed at low temperature in the previous analysis under N_2 atmosphere. The thermal analysis of a fresh sample (shown in Figure 3) reveals that some sulfur was probably still present in the carbon black sample, which was not removed under inert atmosphere at 1273 K, but is eliminated in the form of SO_2 simultaneously with the combustion of the bulk carbon black around 973 K. This

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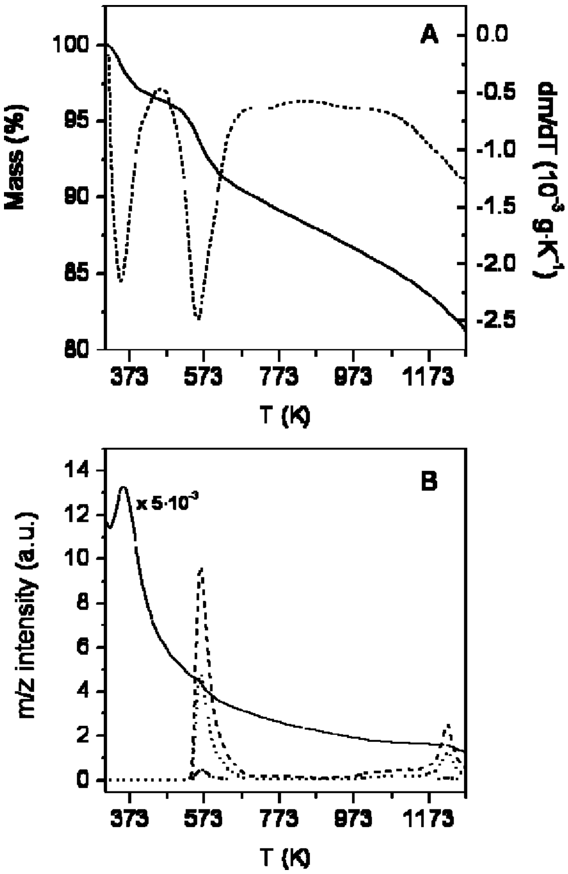

Figure 1. Temperature-programmed desorption of the E-TEK Pt (20 wt %)/Vulcan XC72 catalyst under N_2. (A) Thermogravimetric analysis. Solid line, percentage of mass in the sample; dashed line, differential curve for mass loss. (B) Mass spectrometric analysis of the effluent from TPD: (—) *m/z* = 18, (- - -) *m/z* = 64, (• • •) *m/z* = 48, (- • - •) *m/z* = 66.

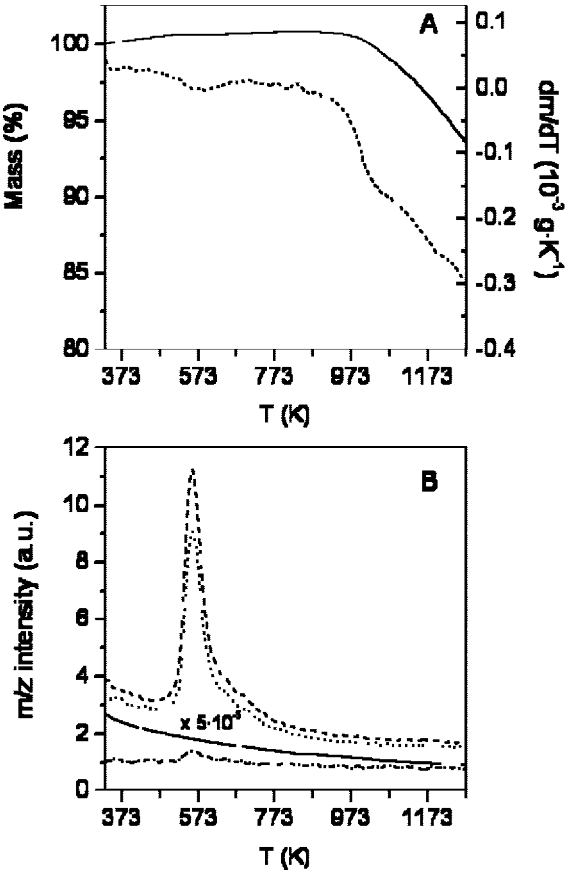

Figure 2. Temperature-programmed desorption of the Vulcan XC72 support under N_2. (A) Thermogravimetric analysis. Solid line, percentage of mass in the sample; dashed line, differential curve for mass loss. (B) Mass spectrometric analysis of the effluent from TPD: (—) *m/z* = 18, (- - -) *m/z* = 64, (• • •) *m/z* = 48, (- • - •) *m/z* = 66.

finding corroborates that SO_2 in the catalyst proceeds (at least in part) from the carbon black support.

A more detailed analysis of the species released from the support by thermal treatment has been performed by mass spectrometry applying a linear ramp of 10 K min^{-1} in the vacuum system up to 773 K, since this system allows much higher sensitivity than the previous analysis in the TG-MS system. Mass-to-charge ratios within a wide range were analyzed to explore the origin and nature of the desorbed gases. Figure 4 presents the ion current evolution for some of the most significant mass-to-charge ratios showing variation during the thermal desorption: among them *m/z* 18, 19, 31, 32, 47, 64, and 69. Desorption of water can be assigned to the ion current for *m/z* = 18, taking place at temperature above 573 K. Although the ion current for *m/z* = 19 contains a contribution from water (0.1%), its profile indicates that it has contribution from a fluorine-containing source. When the contribution of water is subtracted from the ion current for *m/z* = 19, a main peak at 608 K perfectly concurring with that of *m/z* = 31 appears. Ion fragments of mass 31 are typical for the decomposition of fluoride hydrocarbons. The evolution of other ion currents for the masses 32, 47, 64, and 69 are also indicative of the formation of fragments such as S^+ (32), COF^+ (47), $SO_2{}^+$ (64), or $CF_3{}^+$ (69), corroborating the presence of sulfur and fluorine species on the carbon black support.

Probe Molecules (H_2, CO) Chemisorption Study. H_2 and CO chemisorption measurements have been carried out on aliquots of the as-received E-TEK Pt/Vulcan XC72 catalyst after being degassed and thermally treated under vacuum. The effect of the applied temperature on the chemisorption capacity for these two probe molecules has been evaluated. It must be mentioned that a fresh sample was used for each adsorption test. The amount of hydrogen adsorbed on the catalyst is plotted in Figure 5 as a function of the evacuation pretreatment temperature. An enhanced H_2 uptake can be observed after the catalyst is treated at temperatures in the range between 393 and 473 K. Values up to 1.0 mol H_2/mol Pt are obtained corresponding not only to chemisorption on the metal but to other parallel processes. Above those evacuation temperatures, the adsorption capacity of the sample is maintained close to 0.20 mol H_2 per mol of Pt in the catalyst, showing a slight decrease when increasing temperature. By assuming hypothetically that the whole amount of Pt atoms in the metallic state was exposed to the surface and accessible to hydrogen, a maximum of adsorption of 0.50 mol of H_2 per mol of Pt would be achieved. The exacerbated adsorption measured after evacuation at temperatures between 393 and 473 K reveals that hydrogen chemisorption on the Pt catalyst interferes with other surface processes retaining H_2 on the catalyst, which alter the measurement for evaluation of surface Pt. Above 473 K, H_2 adsorption diminishes at a lower rate. At 673 K the H_2 uptake

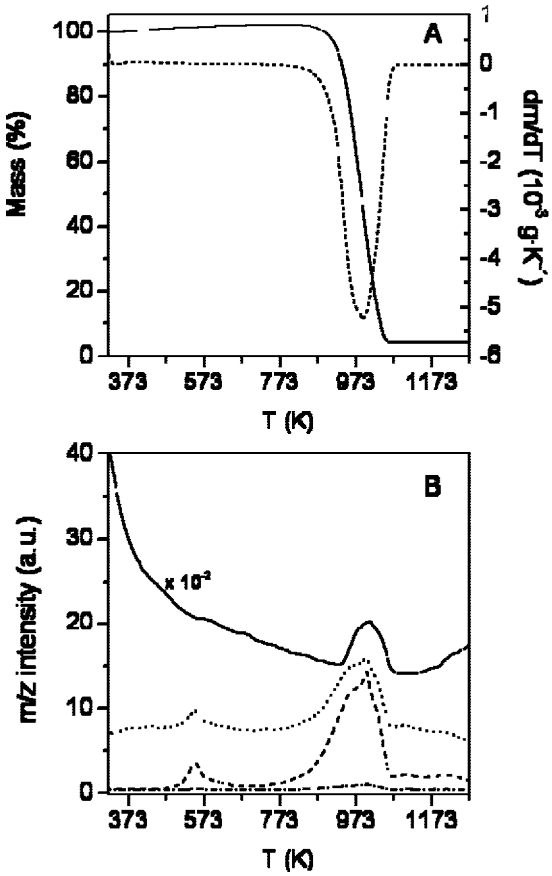

Figure 3. Temperature-programmed oxidation of the Vulcan XC72 support. (A) Thermogravimetric analysis. Solid line, percentage of mass in the sample; dashed line, differential curve for mass loss. (B) Mass spectrometric analysis of the effluent from TPD: (—) $m/z = 18$, (- - -) $m/z = 64$, (• • •) $m/z = 48$, (- • - •) $m/z = 66$.

is reduced by 75% with respect to the uptake at 473 K. It must be mentioned that the H_2 adsorption rate observed on this catalyst has been observed to be relatively slow as compared to the chemisorption rate on a free Pt surface. This slow adsorption rate is probably the cause of the difficulty found for determining chemisorption measurements using a dynamic method of adsorption with injection of H_2 pulses in a continuous Ar flow, from which no H_2 adsorption could be measured. Those conditions do not allow determining the surface Pt using H_2 as adsorption probe.

At those temperatures at which hydrogen adsorption was observed to largely exceed the expected adsorption stoichiometry of 1 mol of hydrogen atoms per mol of surface Pt centers in a static system, a sequence of adsorption cycles was carried out for a given sample. Each cycle included degassing of the sample at 298 K, thermal treatment under vacuum for 2 h and H_2 adsorption at 298 K. After determination of the hydrogen uptake from its adsorption isotherm, the adsorbed hydrogen was oxidized by admitting air in the sample bulb. Then, a new cycle for adsorption was performed after heat treatment at the same temperature. The exposition of the catalyst to oxygen was found to be necessary for removal of the previously adsorbed hydrogen at relatively soft conditions before a new measurement was carried out, because thermal desorption of the chemisorbed hydrogen in platinum-supported catalysts requires much higher temperatures that those of the evacuation pretreatment. Applying very high temperatures could lead to the sintering of the metal particles in the catalyst.[6–19] As a matter of fact, H_2 uptake is significantly reduced when the initial treatment temperature is increased from 473 to 673 K. As shown in Figure 6, the amount of adsorbed hydrogen was also observed to decrease with the number of cycles showing a tendency to reach the adsorption values obtained after evacuation at temperatures above 473 K.

Adsorption isotherms using CO as probe molecule were carried out in a similar way in the static volumetric system after treating the catalyst under vacuum at different temperatures to establish a correlation with the uptakes previously estimated from H_2 adsorption. Obtained values are shown in Figure 7. CO chemisorption does not seem to be much influenced by the pretreatment temperature of the sample because uptake values remain close to 0.23 mol CO per mol of Pt in the catalyst with a subtle tendency to decrease with increasing temperatures.

The Pt surface area has been estimated from the values obtained for H_2 adsorption at 473 K and from CO chemisorption on the catalyst. Data obtained from adsorption are summarized in Table 1. Adsorption stoichiometries of 1:1 and 1:1.5 for H/Pt and CO/Pt have been considered, respectively. The adsorption of CO on platinum typically leads to linearly bonded species associated with atop sites, as well as bridge-bonded species associated with two surface Pt atoms. Thus, the generally used 1:1.5 stoichiometry for CO/Pt approaches the 0.7 value given in literature for the CO monolayer coverage on Pt.[20,21]

To determine if the pretreatment had had any influence in the process of CO adsorption, after equilibration of CO with the catalyst, we evacuated the gas phase from the bulb sample. A TPD was then performed under dynamic vacuum while the increase of pressure in the chamber and the intensity of some m/z ratios of desorbed species were registered with the mass spectrometer. Figure 8 shows the CO TPD profiles obtained for samples of the catalyst pretreated under vacuum at different temperatures. They are presented together with the TPD curve registered for the as-received sample in which no CO adsorption has been performed. It is evident from the large differences among the obtained profiles that the adsorption of CO is greatly modified by the presence of adsorbed species on the catalyst surface, although CO uptakes do not reflect them.

The evolution of CO and CO_2 from the samples has been analyzed during the desorption tests. Their amounts have been estimated from the intensities of the 28 and 44 mass-to-charge ratios registered by the mass spectrometer. Ion intensity for $m/z = 44$ is assigned to CO_2. The CO amount has been calculated from the ion intensity of $m/z = 28$ by

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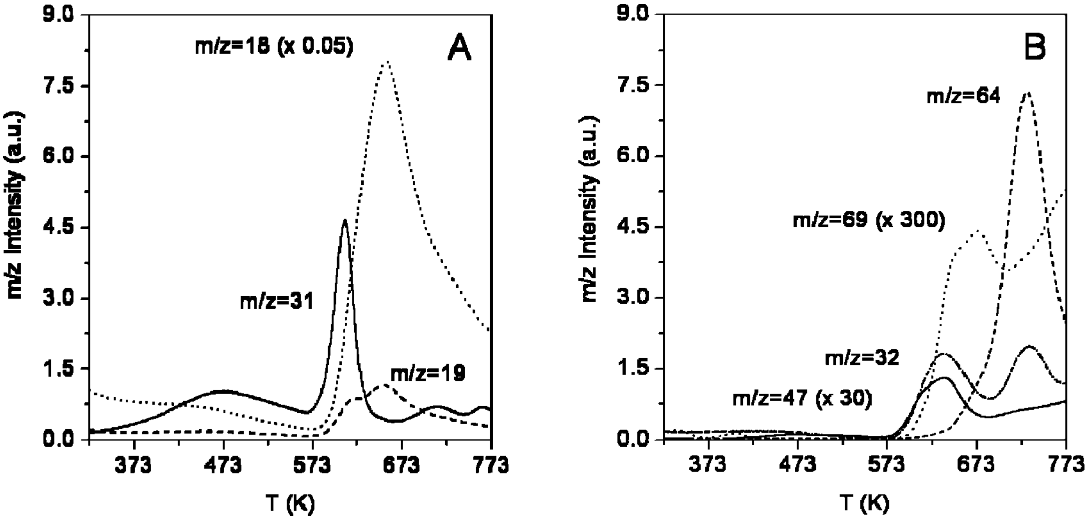

Figure 4. Mass spectra evolution of the desorbed species registered during the thermal treatment of theVulcan XC72 support under dynamic vacuum. (A) (• • •) Ion current for *m/z* = 18 corresponds mainly to water; ion currents for *m/z* = 31 (—) and *m/z* =19 (- - -) show the contribution of F-containing compounds. (B) Ion currents for *m/z* ratios corresponding to S- and F-containing species (—) *m/z* = 47 (×30); (• • •) *m/z* = 69 (×300); (- - -) *m/z*= 64; (• - • -) *m/z* = 32.

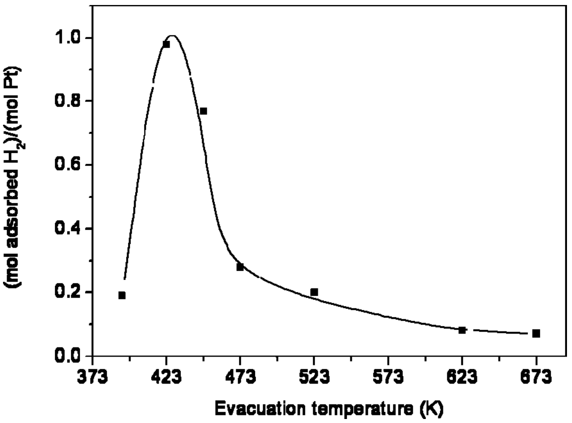

Figure 5. Amount of H_2 adsorbed per mole of Pt for the standard E-TEK Pt (20 wt %)/Vulcan XC72 catalyst as a function of the evacuation temperature.

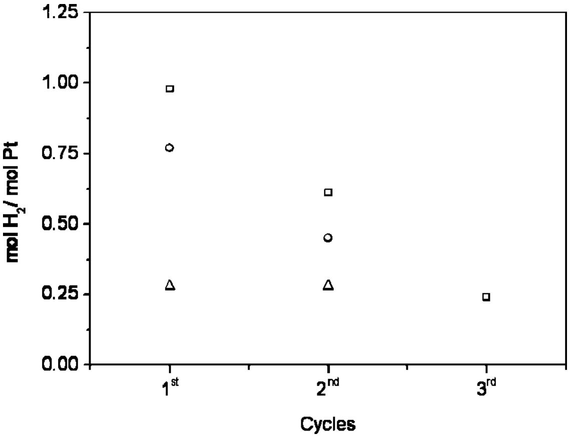

Figure 6. Amount of H_2 adsorbed per mole of Pt for the standard E-TEK Pt (20 wt %)/Vulcan XC72 catalyst after cycles of oxygen adsorption at 298 K and evacuation for 2 h at 423 K (□), 448 K (○), and 473 K (△).

subtracting the contribution to that signal of the CO_2 (*m/z* = 44) fragmentation, which has been estimated to be 11.4%.[22]

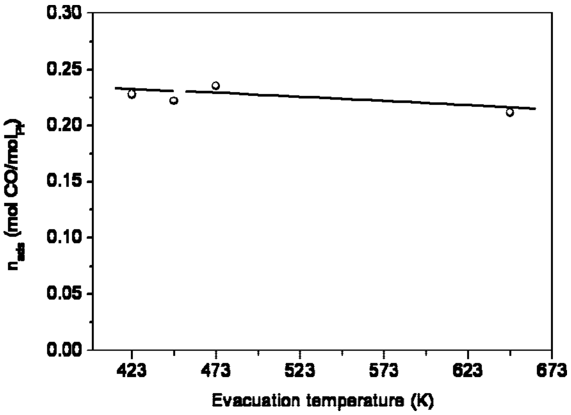

Figure 7. Amount of CO adsorbed per mole of Pt for the standard E-TEK Pt (20 wt %)/Vulcan XC72 catalyst as a function of the evacuation temperature for cleaning the catalyst surface.

Table 1. Adsorption Values for H_2 and CO As Probe Molecules for the Characterization of the Standard E-TEK 20% Pt/Vulcan XC72 Catalyst

T (K)	mol H_2/ mol Pt[a]	m^2_{Pt}/g_{Pt} (H_2)	*d* (nm)	mol CO /mol Pt	m^2_{Pt}/g_{Pt} (CO)[b]	CO/H
498	0.22	119	2.4	0.23	82	0.52

[a] Chemisorption after pretreatment in a vacuum at 473 K. [b] The assumed CO:Pt stoichiometry is 1:1.5.[20,21]

Figure 9 shows the results of CO and CO_2 desorption for the CO equilibrated samples pretreated under vacuum at 473 and 648 K. It must be taken into consideration that there was an evolution of these two species from the as-received catalyst before CO adsorption on the sample. Their desorption profiles are also presented in the same figure as a reference. Two well-defined CO_2 evolution processes take place in the untreated E-TEK catalyst. The first one results in a broad band centered at 523 K. A sharper peak superposed to the former appears at 615 K. CO begins to evolve mainly above 650 K.

For the CO equilibrated sample that was pretreated at 473 K, the species desorbed in major amount is CO_2. It must be

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(22) Mass spectra library from Pffeifer (OmniStar).

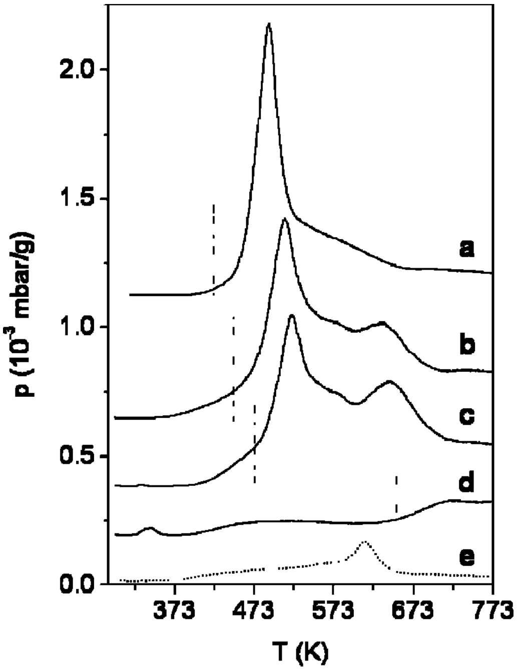

Figure 8. Global desorption profiles of the E-TEK catalyst equilibrated with CO after treatment of the sample in vacuum at (a) 423, (b) 448, (c) 473, and (d) 648 K. The dotted curve is the TPD profile of the "as-received" E-TEK catalyst without pretreatment or adsorption. Vertical lines indicate the temperature at which the catalyst has been pretreated before adsorption.

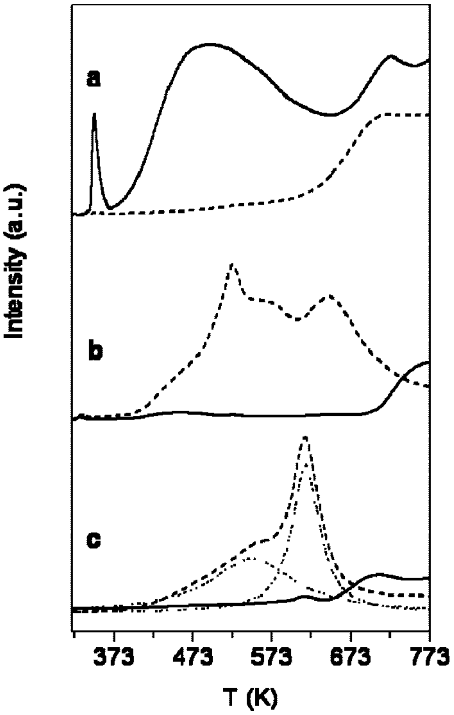

Figure 9. Desorption profiles estimated for CO (solid line) and CO_2 (dashed line) from the mass spectrometer signals for *m/z* ratios 44 and 28 registered during a TPD in vacuum of the E-TEK catalyst equilibrated with CO after pretreatment of the sample in vacuum for 2 h at (a) 648 and (b) 473 K. Curves in (c) correspond to the CO and CO_2 profiles estimated from a TPD of the as-received catalyst without pretreatment or adsorption. Dotted lines represent the deconvolution peaks fitted from the CO_2 profile. $I_{CO} = (I_{m/z=28} - 0.114 I_{m/z=44})$, $I_{CO_2} = I_{m/z=44}$.

considered that before CO adsorption, only a small quantity of the initially present species resulting in CO_2 was removed. After CO chemisorption, the previous bands (which appear at slightly higher temperatures) remain and new peaks for CO_2 evolution appear around 460 and 520 K in addition to a very small contribution at 330 K. It is clear from the results that the catalyst surface after heat treatment under vacuum at 473 K retains oxygen-containing adsorbed species contributing to CO oxidation, which is thermally desorbed in the form of CO_2. The main CO_2 desorption peak at 520 K coincides with similar sharp features for H_2O (ion current for mass 18) and SO_2 desorption from the catalyst (ion current for masses 64, 48, 50, and 66, not shown in the figure).

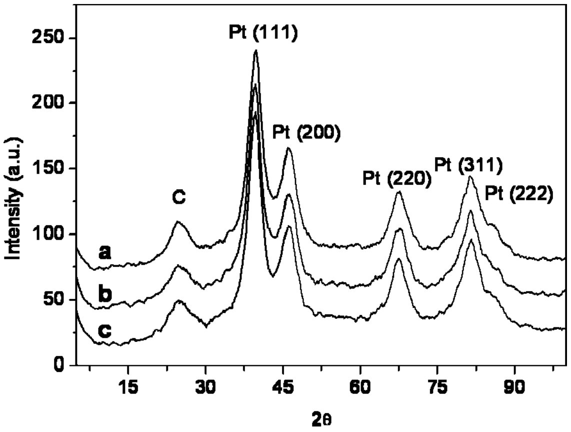

Figure 10. X-ray diffraction patterns of the E-TEK 20 wt % Pt/Vulcan XC72 catalyst treated in vacuum at (a) 448, (b) 523, and (c) 673 K for 2 h.

After heat treatment of the catalyst under vacuum at 648 K, the major part of the previously evolved CO_2 is removed. The Pt surface then seems to be free from other adsorbed species interacting with CO during its adsorption. In this case, CO is the main desorbed product, which evolves from the surface in three main peaks up to 773 K. The two former bands (the peak below 373 K and the band centered at 500 K) can be clearly attributed to the chemisorbed CO on Pt. Above 650 K, CO and CO_2 are probably formed from species previously present in the catalyst.

X-ray Diffraction. To verify if the thermal treatment of the catalyst at temperatures up to 673 K have produced aggregation of the metal particles detectable by X-ray diffraction, samples of the catalysts submitted to thermal treatments in that range were analyzed. The resulting diffractograms in Figure 10 for samples treated under vacuum at 448, 523, and 673 K for 2 h do not allow us to detect any change in the particle size from the width of the Pt diffraction lines.

Discussion

Adsorption of hydrogen from the gas phase on Pt/C is one of the most suitable methods for evaluating and characterizing these catalysts because H_2 adsorption is one of the crucial steps on the anode catalyst within the fuel cell. Hydrogen is dissociatively chemisorbed on clean platinum

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surfaces with a well-defined stoichiometry of one hydrogen atom per surface Pt and is usually chosen as the ideal probe for surface area measurements.[23] Determining the adsorption properties of the standard E-TEK Pt(20 wt %)/Vulcan XC72, which is widely used for research studies, using hydrogen as probe for chemisorption measurements is the key for the correct assessment of other surface measurements based on its adsorption properties, which are usually performed on more complex systems containing the catalyst, such as inks, electrodes, or membrane-electrode assemblies.

This kind of catalyst is usually dispersed on high-surface-area carbons aiming to provide the required electrical conductivity to the system while maximizing its active surface area and avoiding the agglomeration of the metal particles. Ideally, the support acts only as an inert carrier onto which the nanometric metal crystallites are distributed. However, the surface chemistry of the support is in some cases able to confer certain properties to the metals dispersed on it differing from those which are intrinsic of the metal. Hydrogen chemisorption on the standard E-TEK catalyst has revealed some peculiarities for this system, probably related to the surface chemistry of the carbon black in relation to the adsorption of H_2. To obtain the Pt surface free from adsorbed species before chemisorption, the application of a thermal treatment under an inert atmosphere or under a vacuum has been shown to be essential. This treatment must be as soft as possible to avoid structural changes of the metal particles in the catalyst. TPD profiles obtained under an inert atmosphere from the catalyst (Figure 1) and from the carbon black support (Figure 2) have revealed the presence of labile species containing sulfur in the Vulcan XC72 carrier, which are released at 555 K in the form of SO_2 (masses 64 and 48). The application of that temperature was observed to be insufficient for the complete removal of sulfur, and a second SO_2 release was observed when the catalyst was heated at temperatures above 1000 K. The evolution of SO_2 at that temperature seems to be catalyzed by the presence of Pt, because it was not observed when the carbon support was heated under a N_2 flow. However, those species were burned in the presence of oxygen at high temperature together with bulk carbon black (Figure 3). The analysis of ion currents obtained from the mass spectrum of the desorbed products has also unveiled the presence of fluorine as CF_x species not only in the catalyst, but in the carbon black carrier. The modification of the carbon black surface with both species is probably determining the surface chemistry and properties of catalysts using XC72 as support. The TG analysis of the samples also indicates a main difference between the catalyst and the bare support: the release of adsorbed water (almost 4 wt %) from the catalyst surface in a broad range of temperatures up to 473 K.

The presence of sulfur in PEMFC catalysts has been previously reported and attributed to contamination in commercial carbon blacks (CB).[24–26] According to Poleunis et al., the bulk sulfur content in the furnace black XC72 from Cabot Corp. is 0.65 wt %. On the basis of an XPS analysis, they determine at least two different S functional groups: sulfate (HSO_4^-) and thiolate groups (HS^-), although they cannot exclude the presence of other species such as sulfonate (HSO_3^-).[27] As a matter of fact, CBs are usually associated with varying numbers of heteroatoms (H, N, O, F, Na, S, Cl, K, Ca, Si, etc.) that are present in raw materials or introduced during the manufacturing process.[27–29] The functional groups on their surface contribute to their surface reactivity, and the knowledge of the nature of these species is the key to understanding their behavior under different conditions.

The current state of the art on carbon materials focuses almost exclusively on the effect of oxygenated groups that are either present on the carbon surface or can be generated on its surface by oxidation techniques. However, the modification of CBs surface with other heteroatoms such as fluorine is also widespread.[30,31] The physicochemical properties of fluorinated carbon blacks have been shown to be of interest for certain applications. A recent patent from Cabot describes different applications of surface-modified carbons, such as the Vulcan XC-72.[32] Some properties of the modified CBs are especially relevant for their use as catalysts support: the high affinity of metal ions with some functional groups provides anchoring points for a uniform metal distribution and sintering prevention; the wettability of the support can be also modified with ionic or hydrophilic groups for improving the contact with reaction media; selective adsorption of some compounds, thermal conductivity, surface energy, aggregate size, dispersion, viscosity, and chemical reactivity are other parameters that may be altered depending on the chemical modification.

Several Cabot Corp. patents on modified carbons with application in gas diffusion electrodes specify the presence of organic groups attached to the carbon black promoting hydrophobic and hydrophilic characteristics.[33,34] Fluorinated species containing the $-CF_3$ group could be related to the hydrophobicity of the material, whereas sulfonic or carboxylic acid groups could be associated with the hydrophilic character of the surface. It must be taken into account that the initial properties of Vulcan XC-72 CB might be partially modified by treatments to obtain the final E-TEK Pt/Vulcan XC-72 catalyst. Standard E-TEK catalysts are synthesized using the platinum sulfite acid (PSA) as precursor, which is

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first adsorbed on carbon and then reduced. This method that was initially patented by Prototech (from which E-TEK was spun-off) yields catalysts of high surface area and small particle sizes with high loadings. The Prototech patent specifies that although any high surface area carbon is suitable for the synthesis of this type of catalyst, the particular properties of Vulcan XC-72 (Cabot Corp.) as support yield excellent electrocatalysts.[35] According to Petrow et al., SO_2, SO_3, or H_2S can be evolved as result of PSA decomposition during treatments to obtain metallic Pt particles.[35] Tsou et al. stated that the main drawback of this method is the tedious procedure to remove contaminants.[36] Regalbuto et al. have evaluated sulfur removal from catalysts prepared from PSA by dispersing it in different supports.[37] Their study reveals that carbon supported samples, including Vulcan XC72, retain sulfur even after reduction at 573 K. Although, as a matter of fact, the precursor used may contribute to some of the evolved S-containing products during the TPD test, the mass spectra obtained from the thermal analysis of the Vulcan XC-72 and the E-TEK Pt(20 wt.%)/Vulcan XC72 unveils the presence of sulfur surface groups directly attached to the carbon, which are determinant in the catalyst surface chemistry.

It is clear from the results obtained for hydrogen chemisorption on the E-TEK Pt/C catalyst (Figure 5) that the surface chemistry of the support determines the adsorptive properties of the sample. The slow hydrogen adsorption kinetics on this Pt catalyst is probably the result of the chemical modification of the CB. The presence of halides in catalysts has been usually related to the increase of the activation energy for hydrogen adsorption on a metal resulting in slowing down the adsorption process rate at room temperature. Although dynamic adsorption methods of pulse injection on a carrier stream have been shown to fail in the determination of the hydrogen uptake in the E-TEK Pt/C sample because of the slow rate of H_2 chemisorption, the static adsorption measurement method results in uptake values even higher than those that could be attributed to the stoichiometric chemisorption of one H atom per surface Pt center. The enhanced hydrogen uptake seems to be closely related to the presence of water retained on the catalyst, which is progressively removed until SO_2 is released from the most labile sulfur-containing species in the catalyst during the previous treatment of the sample under vacuum in the temperature range between 393 and 673 K. Surface species attached to the support, such as sulfonate groups (HSO_3^-), may act plausibly as acceptors for H_3O^+ ions. By performing several cycles of H_2 adsorption/oxidation on a given sample, the H_2 uptake becomes progressively reduced and the final ratio H_2:Pt tends to reach a value close to that obtained after outgassing the catalyst at 473 K (Figure 6). This is probably the value corresponding just to chemisorption on the surface platinum, which can be used for the surface area estimation. Those cycles of H_2 adsorption/oxidation seem to block the capacity of the sample for the enhancement of H_2 adsorption during the measurement, because dosing O_2 at room temperature is not enough to oxidize those H species interacting with the support, which are usually desorbed at high temperatures. Miller et al. have presented evidence of the oxidation of only those hydrogen species not associated with the spillover effect on alumina support platinum.[38]

Hydrogen chemisorption on Pt probably interferes with protons surface diffusion processes in which the S-containing surface groups of the CB participate. These phenomena of enhanced adsorption can be explained by a hydrogen spillover mechanism, which can be defined as the migration of active species (H_{ads}), adsorbed or formed on a first phase (initiator (Pt centers)), onto another (acceptor), which by itself does not, under the same conditions, adsorb or form those species. Factors influencing hydrogen spillover are relatively well recognized, but some differences concerning their relative influence can be noticed among the literature data.[39] Some of them are the range of temperatures of hydrogen adsorption (below room temperature or significantly above); the possible necessity for a cocatalyst, such as water or other proton acceptors; the amount and the dispersion of the source of hydrogen spillover; or the duration of chemisorption. There are certain systems where slow adsorption may contribute to enhance hydrogen spillover. In those cases, techniques that limit the process kinetically are preferred for surface-area determination. Although in most of the Pt-supported catalysts these diffusion processes usually take place, they do not modify the hydrogen uptake values.[40] In the case of the E-TEK catalyst, dynamic methods do not allow evaluation of the Pt surface area from the adsorbed hydrogen amount at 298 K because of the slow kinetics of adsorption, whereas the static method results in values largely exceeding the monolayer because of hydrogen spillover even at room temperature. This effect had already been reported for fuel cell catalysts.[41,42] Ramirez-Cuesta et al. have provided evidence of this phenomenon by means of inelastic neutron scattering spectroscopy (INSS) on Pt/C, Ru/C, and PtRu/C.[42,43]

A recent patent from Cabot Corp. makes reference to this particularly high hydrogen storage capacity of derivatives from modified CBs, specifying that by tailoring the surface chemistry of these CB materials, the temperature and the equilibrium of the hydrogen adsorption/desorption kinetics on a metal can be altered.[32] According to our results, the

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maximum adsorption capacity is reached after treatment of the sample in vacuum between 410 and 460 K resulting in values close to 1.0 mol of H_2 per mol of Pt in the catalyst. The pretreatment of the sample at 473 K (Figure 1) could be established as the limit temperature for the removal of most of the water adsorbed on the catalyst without significantly modifying the surface carbon groups attached to its surface, which begin to decompose above that temperature, releasing SO_2 as product. Adsorbed water in the catalyst probably acts as cocatalyst for hydrogen surface diffusion and increases the ratio H/Pt with respect to the monolayer. By performing successive H_2 adsorption/oxidation cycles in samples treated at temperatures below 473 K, the H_2 uptake finally converges with the H_2 adsorption value obtained after treatment at 473 K. This result is probably indicating that O_2 dosed at room temperature is only able to oxidize the hydrogen species associated with the metal surface, which restore its capacity to adsorb H_2.

After 2 h treatment in vacuum at 473 K the H_2 uptake at 298 K corresponds to a Pt dispersion of 44% (H/Pt ratio: 0.44). As shown in Table 1, this H_2 uptake corresponds to a Pt surface area of 119 m^2/g with an average particle size of 2.4 nm. These values are in agreement with the specifications of the product supplier resulting from TEM analysis. According to our results, the treatment of the catalyst at temperatures above 473 K significantly lowers the H/Pt ratios. After treatment at 673 K, the H_2 uptake measured is 75% lower than the value measured after treatment at 473 K.

Using CO as alternative probe for the evaluation of Pt surface appears as a more confident measurement, which seems to be practically unaffected by the temperature at which the sample has been previously treated. CO uptake values at 298 K remain close to 0.23 mol CO per mol of Pt in the catalyst, with a subtle tendency to decrease with increasing temperatures that resembles the decrease in hydrogen adsorption above 473 K. However, it must be considered that the different adsorption modes of CO on metal surfaces confer some uncertainty to the measurement. The distribution of the CO adspecies, linearly or bridge-bonding, depends on geometric, structural, electronic, and chemical factors that modify the average adsorption stoichiometry of CO on Pt.

The CO saturation limit is usually established at 0.7 monolayers (ML) for Pt catalysts showing adsorptive properties of the Pt (111) face.[20,21] Usually, the monolayer is referred to the hydrogen adsorption as standard probe. This saturation CO/H ratio of 0.7 is usually found in the literature for supported Pt particles with low or no interaction with the supports showing adsorption surface properties of Pt(111).[21] Cuesta et al. [44] and Gómez et al.[45] have shown that adsorption of CO on platinum *hkl* planes does not lead to a monolayer, the surface coverage by CO being close to 0.65[46] or 0.68[47] for the (111) plane and close to 0.78[48] or 0.82[46] for (110) and (100) planes. Deviations from this value have been observed for catalysts showing modified adsorption properties because of particle-size effects, interactions with the support, or formation of surface alloys.[49,50] According to Table 1, after treatment of the sample at 473 K, the CO/H ratio obtained is 0.52, showing a strong alteration of the adsorption properties of the catalyst with respect to Pt (111) faces.

According to the results published by Zhang et al., adsorption of H_2 and CO on a Pt/Vulcan XC72 catalyst that has been synthesized by simply impregnating Vulcan XC72 carbon black with a solution (ethanol, benzene) of the Pt precursor salt does not reveal any modification of the adsorption properties of platinum with respect to Pt (111).[49] They found a CO/H ratio of 0.7 on a Pt/Vulcan XC72 catalyst with low metal loading (2 wt %), determining H_2 and CO chemisorption values in an analogous volumetric system with a similar procedure[49] (samples were reduced at 573 K and outgassed at 673 K before adsorption).

According to the uptake values measured for CO, its adsorption on the catalyst seems to be unaffected by the sample pretreatment. However, large differences become apparent for CO chemisorption on the catalyst when analyzing its TPD profiles (Figure 8 and Figure 9). CO desorption from Pt (111) takes place in the range between 320 and 550 K in a broadband with no resolution of peaks.[51] This broad CO desorption band appears only for the catalyst pretreated at temperatures above 473 K, together with a sharp desorption peak below 373 K corresponding to weakly adsorbed CO (Figure 9a). A third desorption band above 673 K is due to CO species derived from the thermal decomposition of surface groups in the Vulcan XC72 support. It must be noted that there is some evolution of CO_2 and CO from the as received catalyst without any treatment (Figure 9c).

CO_2 is mainly evolved from the untreated catalyst up to 673 K in two bands: the first one is centered at 523 K and the second and sharper is superposed at 615 K. This CO_2 evolution profile results significantly modified after CO adsorption on the sample that had been previously treated at 473 K. The main striking feature in the TPD is that CO_2 is the main desorption product even at low temperatures, indicating that surface species remaining on the catalyst after treatment at 473 K are able to oxidize practically all the adsorbed CO. The two well defined bands in the CO_2 profile obtained from the TPD of the as-received catalyst are transformed in at least 5 peaks indicative of the different sites for CO adsorption and reaction.

These results indicate that CO adsorption is also strongly influenced by the surface chemistry of the support in the E-TEK catalyst, although the CO uptake values obtained at

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increasing treatment temperatures do not reflect it clearly. The CO and CO_2 profiles in the TPD from samples equilibrated with CO after treatment at moderate temperatures (473 K) show that CO is not chemically adsorbed on a clean Pt surface, but interacts with other species in the catalyst able to oxidize it to CO_2. Although one could expect that those interactions might increase or reduce the CO uptakes as result of the different adsorption modes of the formed adspecies, only a slight decrease in the adsorbed amount is detected. By considering that the XRD analysis of the treated samples does not reveal any significative change or broadening of the Pt diffraction lines, one must conclude that heat treatment up to 673 does not lead to large changes in the average crystallite size. Thus, by considering that after treatment at 673 K, the H_2 uptake is reduced by 75% with respect to that obtained at 473 K, the high CO/H ratios found on samples treated at temperatures above 473 K are probably indicating the inhibition of H_2 chemisorption on Pt under those conditions. The relatively clean CO desorption profile resulting from the catalyst treated at a relatively high temperature (648 K) and resembling that of a clean Pt surface (Figure 9a) together with the fact that no broadening of the Pt XRD lines is detected (Figure 10) supports the argument of the absence of metal sintering with the applied temperature. The large decrease in H_2 uptake when the treatment temperature is increased can be attributed to the inhibition of its adsorption as a result of the decomposition of the fluorinated groups from the support. The stronger adsorption of CO on Pt as compared to H_2 makes CO uptake measurements less sensitive to the presence of elements modifying the Pt adsorption properties, such as the halides.[52]

A certain parallelism with these results can be found in the study of Cai et al. concerning the thermal and electrochemical degradation of PEMFC catalysts.[19] Their work shows that heat treatment in an inert atmosphere at 523 K of two commercial TKK Pt catalysts supported on carbon black Vulcan XC72 and on a large-surface-area carbon does not cause sintering of Pt, as revealed from the broadening of the Pt XRD lines. Their surface area, as determined from dynamic chemisorption measurements of CO pulses for the heated samples under an inert atmosphere, did not reveal any area loss, but an increase in the CO uptake after heat-treatment as compared to the initial amount obtained for the fresh catalysts. They attributed the enhancement in the Pt active surface area in the samples treated under flows with O_2 levels below 0.05% to the removal of impurities adsorbed from carbon onto Pt by reaction with oxygen. It must be considered that they submitted the samples to a H_2 flow for 30 min at 373 K before chemisorption, and that temperature is probably too low for removal of adsorbed species from the Pt surface in the as-received catalysts. Then, after treatment at higher temperature, the Pt surface probably adsorbs more CO as a result of the desorption of adspecies blocking surface Pt sites. According to their results, the presence of H_2O and/or O_2 above certain concentration levels induced in them a loss of area and an increase in the crystallite size as determined by XRD, mainly because of corrosion of the carbon support. It must be considered that their treatment may modify the surface chemistry of the supports and slightly alter the Pt adsorption properties with time on stream. As a matter of fact, Kangasniemi et al. have recently presented evidence of surface oxidation of the Vulcan XC-72 carbon black under simulated PEMFC conditions, which may contribute to the change in hydrophobicity of the electrodes.[53] They have presented a detailed analysis of the evolution of CO and CO_2 from electrodes made from Vulcan XC-72/PTFE, showing that changes in their hydrophobicity resulting from the formation of surface groups are an important factor in determining their long-term performance instability and decay.

The influence of the treatment temperature on the structure of Pt crystallites in catalysts seems to depend on the surrounding atmosphere. Thermal treatment under vacuum or any other inert atmosphere at moderate temperatures (below 673 K) does not seem to affect the particle size of this type of samples. However, thermal reduction at 473 K under a pure H_2 stream or H_2 diluted in an inert carrier gas leads to the aggregation and sintering of the carbon supported Pt with a kinetics that depends on the temperature range or the atmosphere composition.[6,19]

The results presented in this work evidence the large influence of the surface chemistry of the support on the adsorptive properties of the standard E-TEK Pt(20%)/XC72 catalyst. Although a large amount of data related to this commercial catalyst, the XC72 carbon black and several components manufactured from them can be found in literature, a detailed analysis of their properties concerning their physical-chemical characterization were lacking. A deeper knowledge of the factors affecting the surface chemistry and the basic adsorption processes of H_2 and CO on this widely used electrocatalyst is a key step in establishing basic criteria for the correct evaluation of the surface area on the basis of chemisorption measurements. This is a fundamental point to standardize the surface area measurements for electrocatalysts. Characterization of PEMFC components such MEAs, electrodes, or inks requires taking into consideration the adsorptive properties of the base catalyst that these elements contain in order to correctly assess surface area values estimated from adsorption measurements on them. Understanding the mechanisms of the adsorption processes and knowing the factors contributing to their enhancement or inhibition are essential in designing tailor-made electrodes of high performance, with improved properties and with reduced Pt loadings.

Beyond the particular characteristics of the commercial catalyst evaluated in this study, the combination of H_2 and CO adsorption measurements on a clean catalyst surface previously treated under vacuum conditions provide a useful tool for exploring adsorptive properties of any kind of PEMFC catalyst. Generally, a simplified picture of stoichiometric adsorption of molecules such as H_2 and CO on surface Pt centers is used to estimate the metal surface area.

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However, mechanisms of adsorption, surface reaction, and desorption may become extremely complex, especially over supported catalysts, where parasitic phenomena due to the interaction between the active phase and the support can interfere. Then, their behavior may greatly differ from unsupported Pt crystallites. The results obtained for the studied catalyst address a series of arguments that are important in explaining the performance and stability of PEM fuel cells and establishing a series of criteria for correct assessment surface area measurements. First, thermal treatments of components containing surface-modified carbons, such as Vulcan XC72, may cause modification of the adsorption behavior of the Pt catalyst resulting from the decomposition of the carbon surface functional groups. In a similar way, these groups, which may contain heteroatoms such as H, N, O, F, Na, S, Cl, K, Ca, Si, etc., may also become degraded or oxidized during operation of MEAs or the characterization of their components. Degradation of other materials such as PTFE or PFSA, which are usually present on the electrodes, might cause a similar effect. The relevance of some carbon surface groups on the hydrophilic and hydrophobic properties of the catalytic layer and their fundamental role in the mass transport across the catalytic layer are other points to consider. Further analysis of these issues is required to determine the most suitable methods and conditions to evaluate “real surface areas” in electrodes, because different surface analysis techniques may not result in a catalyst surface area that is representative of the actual useable Pt surface in the catalyst when it comes to hydrogen oxidation and oxygen reduction.

Conclusions

The commercial E-TEK standard Pt (20 wt %)/XC72 has been characterized to determine its surface metal area by means of H_2 and CO chemisorption. Thermal desorption studies on the catalyst and the support unveil the presence of functional groups modifying the carbon black surface. Those species directly attached to the support surface contain sulfur and fluorine as heteroatoms conferring hydrophilic and hydrophobic properties to the carbon surface. These species contribute to modify the adsorption properties of the catalyst with respect to those of Pt. The kinetics of H_2 adsorption on this catalyst has been observed to be slower as compared to that usually observed on other supported Pt catalysts or on the bare metal, probably because of the presence of fluorine. The slow kinetics difficults the measurement of the H_2 uptake using dynamic adsorption methods. Static measurements by means of a volumetric adsorption system have revealed that some functional groups present in the XC72 support participate in enhancing the H_2 uptake. This enhanced adsorption seems to be related to hydrogen adsorption–diffusion processes cocatalyzed by H_3O^+ ions, probably associated with hydrophilic sulfonic groups in the carbon black surface. H_2 uptake measurements mainly corresponding to chemisorption on the metal are obtained after outgassing the catalyst at a temperature high enough to remove adsorbed water from the catalyst surface without removing the most labile sulfur- and fluorine-containing groups in the support (i.e., 473 K). The same H:Pt ratio can also be obtained after several H_2 adsorption–oxidation cycles outgassing the sample at lower temperatures. CO uptake values in the catalyst are not dependent on the outgassing temperature of the sample, although its adsorption on the catalyst is also strongly influenced by the surface chemistry of the carbon black, as revealed by the thermal desorption studies. These factors affecting the surface chemistry and basic adsorption processes of H_2 and CO on this widely used electrocatalyst are the key to establishing basic criteria for the correct evaluation of its surface area on the basis of chemisorption measurements.

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