Influence of the nature of the carbon support on the activity of Pt/C catalysts for ethanol and carbon monoxide oxidation

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Abstract

The electrooxidation of ethanol and carbon monoxide on Pt nanoparticles supported on different carbon materials (nanofibers, CNF, and carbon blacks) was studied. Quite similar characteristics were found for Pt, including particle size and crystal phases, regardless the nature of carbon support. Cyclic voltammetries and current-transient curves showed higher ethanol oxidation current density for Pt/CNF than for Pt/Vulcan. *In situ* spectroelectrochemical techniques including Fourier transform infrared spectroscopy (FTIR) and differential electrochemical mass spectrometry (DEMS), were employed in order to identify adsorbed reaction intermediates and products and volatile reaction products, respectively. Pt supported on CNF resulted in a lower CO poisoning of the Pt surface compared to Pt/Vulcan, allowing higher amount of free Pt active sites for the oxidation of ethanol, leading to the formation of acetic acid during the reaction.

1. Introduction

The development of direct ethanol fuel cells (DEFCs) is very attractive because of the necessity to supply alternatives to petroleum as energy vector. Ethanol is a very promising organic liquid fuel because it can be obtained from the fermentation of biomass in large quantities (renewable), it is not toxic like methanol and has a high specific energy of 8.01 kWh kg⁻¹ [1] and [2], which is comparable to that of gasoline. Pt

is considered the best monometallic catalyst toward ethanol oxidation reaction (EOR), however, the oxidation of the fuel involves the formation of intermediates (CO-like species) that strongly adsorb on Pt active sites resulting in the inactivation of the catalyst [3]. The latter, in combination with the scarcity and high cost of Pt, has seriously impeded the commercialization of such devices.

One important aspect to consider is the catalyst metal support since it plays a key role in the electroactivity toward EOR. Carbon materials are the most employed metal supports because they are able to provide a good electrical conductivity, suitable dispersion of metal particles and appropriate resistance to acid and basic media. Many research groups have recently been working with different novel carbon supports such as nanotubes [4], [5], [6] and [7], nanofibers [8], [9] and [10], carbon xerogels [11] and [12], and mesoporous carbons [13] and [14] for fuel cell applications.

Trying to understand the pathways and potential mechanisms for the EOR is a challenge that has been reflected in many articles [15] and [16], owing to the number of possible steps that can take place. The cleavage of the C–C bond of ethanol, in particular, presents a considerable challenge that is not present in the oxidation of smaller molecules such as formic acid or methanol. *In situ* spectroscopic methods are useful for studying the complex electrochemical mechanism occurring during the oxidation of ethanol. Increasing attention has been paid to modern spectroscopy techniques as *in situ* Fourier transform infrared spectroscopy (FTIR) and differential electrochemical mass spectrometry (DEMS) techniques [17] and [18].

In this work, Pt catalysts supported on CNFs and Vulcan were prepared by formic acid reduction method (FAM) [19], and their electrochemical behavior toward CO and ethanol electrooxidation reactions were studied. The catalytic performance of Pt/C catalysts was evaluated by cyclic voltammetry, and current–time curves, as well as

spectroscopic methods adapted to the electrochemical systems for *in situ* studies. The aim of the present work is to elucidate different electrochemical behaviors and mechanistic insights influenced by the carbon support.

2. Experimental

2.1 Catalysts preparation

Oxidized Vulcan (labeled as Vulcan NSTa0.5) has been prepared by oxidation of carbon black (Vulcan XC-72R, from Cabot Co.) with concentrated nitric and sulfuric acids (Sigma Aldrich) at room temperature during 30 min under stirring and refluxing conditions [20]. Carbon nanofibers (CNF) were obtained by the catalytic decomposition of methane on a nickel-based catalyst ($\text{NiCuAl}_2\text{O}_3$) at 750°C [21]. Pt was supported on the different carbons by using the formic acid method as described in the literature [19]. H_2PtCl_6 (Sigma-Aldrich) was employed as metal precursor and the appropriated amount of this salt was used in order to obtain nominal metal loading of 20 wt% in all cases.

2.2 Physicochemical characterization

X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS), were employed for the physicochemical characterization of all catalysts.

Powder XRD patterns of Pt/C catalysts were recorded in a Panalytical X'Pert diffractometer using $\text{Cu-K}\alpha$ radiation. Scans were collected at 3° min^{-1} for 2θ values between 20° and 100° .

The XPS analyses were performed with a VG-Microtech Mutilab 3000 spectrometer equipped with a hemispherical electron analyzer and a $\text{MgAl}\alpha$ X-ray source. The

constant charging of the samples was corrected by referencing all energies to the C_{1s} peak at 284.6 eV.

Pt metal loading was determined by EDX, coupled to a scanning electron microscope (SEM) LEO Mod. 440.

2.3 Electrochemical characterization

An electrochemical cell with three electrodes was used for the electrochemical characterization. The working electrode consisted of a glassy carbon disk (7 mm) where an aliquot of the catalyst ink was pipetted and dried at ambient temperature under N₂ atmosphere on the top. The ink was prepared by ultrasonically dispersing 2 mg of the catalysts in 0.5 mL of ultrapure water (Millipore) and 15 μ L of Nafion (5 wt%). A high surface area carbon rod was used as counter electrode and a reversible hydrogen electrode (RHE) in the supporting electrolyte was employed as reference electrode. All potentials will be referred to this electrode.

0.5 M H₂SO₄ (Merck p.a.) aqueous solution was employed as support electrolyte. The electrolyte was deaerated with pure Ar (99.998%, Air Liquide). When necessary, ethanol (Merck p.a.) was subsequently added to the support electrolyte for a concentration of 1 M.

The CO oxidation was studied by stripping experiments. First, CO (99.997%, Air Liquide) was bubbled to the support electrolyte for 10 min while polarizing the electrode at 0.07 V vs. RHE; then removing non-adsorbed CO by bubbling Ar for 20 min; and finally, scanning the potential up to 1 V vs. RHE at 20 mV s⁻¹.

Cyclic voltammograms (CVs) and current transient curves were obtained in the presence of 1 M ethanol. CVs were recorded at 20 mV s⁻¹, whereas chronoamperometries were recorded during 600 s obtained by stepping the potential

from 0.05 V vs. RHE (potential in which ethanol is not oxidized) to 0.55 V vs. RHE (potential close to that in a DEFC).

2.4 Spectroelectrochemical characterization

Differential electrochemical mass spectrometry (DEMS) method details and cell designs have been reported in the literature [22] and [23]. For detection of the ion current during mass spectrometric measurement, Balzers Omnistar quadrupole mass spectrometer was used. A conventional electrochemical cell was used and the meniscus configuration was adopted. The working electrode consists of a glassy carbon disk (7.0 mm of exterior diameter, SIGRADUR® G) with an inner cavity of around 1.5 mm of diameter, where a PTFE membrane (Scimat) is accurately placed allowing the detection of volatile and gaseous products and intermediates generated in the electrochemical reactions with excellent sensitivity. The experimental setup allows the simultaneous acquisition of mass spectrometric cyclic voltammograms (MSCVs) for selected masses, and conventional voltammograms (CVs) recorded at a scan rate of 0.005 V s^{-1} .

In order to determine the efficiency of the ethanol conversion to CO_2 , the determination of the $m/z = 22$ calibration constant (K_{CO_2}) is necessary. This constant correlates the number of CO_2 molecules generated on the electrode surface (through the faradaic charge) with the portion of this molecules captured by the mass spectrometer (proportional to $m/z = 22$ ion current). K_{CO_2} has to be determined before each experiment because it depends on several variables (membrane-electrode gap, flow rate, temperature and pressure in the mass vacuum line). The calibration constant is calculated as follows:

$$K^{\text{CO}_2} = 2 \frac{Q_i^{\text{CO}_2}}{Q_f^{\text{CO}_2}}$$

Faradaic (Qf^{CO_2}) and ionic $m/z = 22$ (Qi^{CO_2}) charges were calculated from CO stripping. This constant was employed to determine the CO₂ conversion percentage, employing the following equation:

$$E^{CO_2} = \frac{6 * Qi^{CO_2}}{K^{CO_2} * Qf^T}$$

where Qf^T corresponds to the faradaic charge produced during the ethanol oxidation.

In-situ Fourier transform infrared spectra (FTIRS) were collected with a Bruker Vector 22 spectrometer equipped with a homemade spectroelectrochemical glass cell with a 60° CaF₂ prism at the bottom. It was designed for external reflection mode in a thin layer configuration. FTIR spectra were acquired from the average of 128 interferograms, obtained with 8 cm⁻¹ resolution at selected potential, by applying 0.05 V single potential steps from an initial potential ($E_0 = 0.05$ V vs. RHE) in the positive direction up to 0.8 V vs. RHE. Spectra are represented as the ratio R/R_0 , where R and R_0 are the reflectance measured at a given potential and the one measured at the initial potential E_0 , respectively. Consequently, positive and negative bands correspond to the loss and gain of species at the sample potential, respectively.

3. Results and discussion

3.1 Electrocatalysts physicochemical characterization

Figure 1 shows the XRD patterns of the three Pt/C catalysts, including the identification of the typical face centered cubic (fcc) crystalline peaks of Pt, namely (111), (200), (220), (311) and (222), and the graphitic reflection plane of carbon support (002) at $2\theta = 24.5^\circ$. The latter is significantly higher for CNF compared to the carbon blacks Vulcan XC-72R and Vulcan NSTa0.5, reflecting the high graphitization degree of CNF.

As can be seen in table 1, Pt crystallite size, calculated from the Scherrer equation and the broadening of the Pt (220) reflection, results in similar values, for platinum nanoparticles supported on Vulcan around 3.5-3.8 nm, and slightly higher for Pt supported on CNF (5.3 nm). Pt lattice parameter, determined from the Bragg equation, was quite close to 3.92 Å for all of them, value generally assigned to platinum supported on carbon. The metal loading of the catalysts was determined by EDX, showing approximately 20 wt% of Pt in all Pt/C catalysts, regardless the carbon support employed.

The Pt 4f XP spectra for the all catalysts are shown in Figure 2. These spectra can be deconvoluted into three contributions ascribed to Pt (0), Pt (II) and Pt (IV) species, which appear at ca. 71.4, 72.4 and 74.1 eV, respectively. Table 2 summarizes the results regarding the deconvolution of Pt 4f peaks. The results reflect that Pt is mostly in its reduced state in all catalysts (63-72%). The catalyst supported on CNF showed the lowest amount of metallic Pt, while the one supported on oxidized Vulcan (NSTa0.5) exhibited the highest amount of Pt (0), revealing that, although Vulcan NSTa0.5 is the carbon with the highest amount of oxygenated groups on its surface within the three studied supports [10], it appears that Pt is not oxidized by such groups. Other interesting feature is that the weight percentage of carbon on the surface (57%) was significantly lower than nominal (80%) when CNF was the support employed, as can be seen in Table 2. This fact evidences that the metal particles are more exposed on the surface of CNF compared to the other two carbon supports. An increased metal content on the surface may provide a higher density of catalytic active sites where ethanol molecules can react, and consequently a better performance of CNFs-based catalysts could be expected.

3.2 CO electrooxidation

CO-stripping voltammetry was used to characterize the catalyst surface as well as to establish their tolerance towards CO poisoning. Figure 3 shows the cyclic voltammograms for all catalysts at 5 mV s^{-1} , including the second cycle, which corresponds to the voltammogram in the base electrolyte (deaerated $0.5 \text{ M H}_2\text{SO}_4$), and the corresponding mass spectrometric cyclic voltammograms (MSCVs) for CO stripping. The mass to charge (m/z) ratio $m/z = 44$ corresponds to the ion current of $[\text{CO}_2]^+$ and the $m/z = 22$ to doubly ionized carbon dioxide $[\text{CO}_2]^{++}$. Prior to the stripping, CO was adsorbed at 0.07 V vs. RHE . The current density (j) is normalized by the electroactive surface area, determined from the electrooxidation of a CO adsorbed monolayer. Two clear CO oxidation peaks for Pt/CNF at 0.66 V vs. RHE and 0.75 V vs. RHE were observed. MSCVs of Figure 3a indicated that not all CO was oxidized after the first peak since no significant ion current signal appeared, suggesting a restricted or slow CO surface diffusion toward the different Pt reactive sites. However, the CVs for the other two carbon supports (Vulcan-based) revealed absence very small contribution of the first peak at 0.66 V vs. RHE whereas the second peak rose and shifted to 0.77 V vs. RHE . It was also observed that the onset potential for CO oxidation took place at practically the same potentials for all the catalysts (around 0.4 V vs. RHE). However, taking into account the anodic charge developed at 0.66 V vs. RHE and the position of the main CO oxidation peak at 0.75 V vs. RHE it can be concluded that Pt supported on CNF allows the highest tolerance to CO poisoning.

The *in situ* FTIR technique was also employed for the investigation of the CO oxidation process on Pt/C catalysts. Figure 4 shows sequences of *in situ* FTIR spectra recorded during CO electrooxidation on Pt/CNF, Pt/Vulcan and Pt/Vulcan NSTa0.5 catalysts while varying the electrode potential stepwise from 0.05 to 1.0 V vs. RHE ($E_0 = 0.05 \text{ V}$

vs. RHE). The bipolar band located at *ca.* 2029 cm^{-1} is ascribed to linearly bonded O-C and the band at 2342 cm^{-1} is attributed to the O-C-O asymmetric stretching mode.

As can be seen in Figure 4, the initial bipolar feature of the CO band became a monopolar band at 1.0 V vs. RHE for Pt/Vulcan NSTa0.5. However, for Pt/Vulcan XC-72R and Pt/CNF the initial bipolar band was still bipolar at this potential. The latter suggests that on the catalysts based on Vulcan XC-2R and CNF, CO_{ad} was still retained in the structure of the catalyst, whereas the diffusion of CO_{ad} was faster in the catalyst supported on Vulcan NSTa0.5. The latter can be attributed to the higher amount of oxygenated groups on the surface of Vulcan NSTa0.5 [10] which favored the oxidation of CO_{ad} .

The potential dependence of the band intensities for the signal at 2342 cm^{-1} is given in Figure 5. The graph reveals that the onset for CO_2 formation on Pt/CNF catalyst took place at lower potentials (*ca.* 0.3 V vs. RHE) than on Pt/Vulcan NSTa0.5 (*ca.* 0.35 V vs. RHE) and Pt/Vulcan XC-72R (*ca.* 0.4 V vs. RHE). Thus, CNF is the support that leads to a higher tolerance to CO poisoning, which is in agreement with DEMS and CVs results.

3.3 Ethanol electrooxidation

Ethanol electrooxidation reaction (EOR) was studied on Pt catalysts supported on CNF, Vulcan XC-72R and Vulcan NSTa0.5 by cyclic voltammetry at room temperature. The working electrode was introduced into the solution at 0.05 V vs. RHE and then a cyclic voltammogram was recorded up to 1 V vs. RHE at 20 mV s^{-1} . The stable profiles (corresponding to the third cycle) are shown in Figure 6a for the three catalysts. Currents were normalized by the electroactive surface area calculated from CO stripping experiments. The best electro-activity toward EOR was found on the Pt/CNF

catalyst, followed by Pt/Vulcan NSTa0.5. Current transient curves (Figure 6b) showed the same trend of EOR electro-activity among catalysts as in the cyclic voltammograms, confirming that it follows the tentative order:

$$\text{Pt/CNF} > \text{Pt/Vulcan NSTa0.5} > \text{Pt/Vulcan XC-72R}$$

DEMS studies were used to provide information on the nature of the gaseous and volatile intermediates and products during the ethanol oxidation on the different electrocatalysts. Cyclic voltammograms (CVs) and the corresponding mass spectrometric cyclic voltammograms (MSCVs) are shown in Figure 7 for ethanol oxidation on Pt/CNF, Pt/Vulcan XC-72R and Pt/Vulcan NSTa0.5 catalyst. Since the $m/z = 44$ corresponds to the ion current of $[\text{CO}_2]^+$ and $[\text{CH}_3\text{CHO}]^+$, the formation of CO_2 and acetaldehyde were selectively investigated by monitoring the $m/z = 22$ ($[\text{CO}_2]^{++}$) and $m/z = 29$ ($[\text{COH}]^+$, main fragment of acetaldehyde), respectively. Whereas, the $m/z = 15$ was monitored to individuate methane and/or to other ionic fragment of acetaldehyde formation ($[\text{CH}_3]^+$). Besides, due to the low volatility of acetic acid (low concentration in the electrolyte solution), no potential dependence for $m/z = 60$ signal could be detected. However, acetic acid can be indirectly detected by ethylacetate ester formation during the reaction monitoring the fragment at $m/z = 61$ $[\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}_2]^+$. As it can be observed in Figure 7, generally $m/z = 22$ signal, ascribed to CO_2 formation, was lower and occurred at more positive potentials than the signals associated to acetaldehyde ($m/z = 15, 44$ and 29) in the anodic going scan, which suggests that the complete oxidation of ethanol to CO_2 is not dominant. Comparing the MSCVs for the three different catalysts during EOR it can be observed that the signal for $m/z = 15$ at potentials below 0.2 V, which is associated with methane formation, was quite higher on Pt/Vulcan than on Pt/CNF catalysts. This fact, in combination with the lower intensity of the signals associated to acetaldehyde ($m/z = 15, 44$ and 29) and acetic acid

($m/z = 61$) in the backward scan on Pt/Vulcan, suggests that the incomplete EOR via acetic acid and/or acetaldehyde is more dominant when CNF is the carbon support. Noticeable was the lower formation of CO_2 and methane with the functionalization of Vulcan. It can be explained because of the higher amount of oxygenated groups on Vulcan NSTa0.5, which favored the incomplete ethanol oxidation.

Table 3 shows the CO_2 conversion efficiency from the faradic and ion-charge integrations during the forward scans of the CV and MSCV, calculated from the $m/z = 22$ (due to a CO_2 formation) signals after a calibration procedure, which allows a more accurate comparison between the catalysts. The difference in area between experimental and theoretical faradaic currents is ascribed to the extra charge associated with the formation of different products other than CO_2 (e.g. acetaldehyde and acetic acid), and therefore, the CO_2 conversion efficiency was estimated. As can be seen, CNF-based catalyst showed the lowest conversion efficiency of ethanol to CO_2 , whereas, the Vulcan-based catalyst presented the highest conversion.

Figure 8 shows FTIR spectra for Pt/CNF, Pt/Vulcan, Pt/Vulcan NSTA0.5 catalysts acquired during successive potential steps (100 mV each) between $E = 0.05$ and 1.0 V vs. RHE in 0.1 M $\text{HClO}_4 + 1$ M ethanol. The band at 2029 cm^{-1} at the binary catalyst is assigned to IR adsorption by linearly adsorbed CO on Pt (Pt-CO), which is produced by the dissociative adsorption and oxidation of ethanol on the electrocatalyst surface. The negative band at ca. 2342 cm^{-1} is associated to the asymmetric stretching vibration of CO_2 . Also, the band at around 1720 cm^{-1} (C=O) is assigned to the $\nu(\text{C-O})$ stretching mode of the carbonyl groups in both acetaldehyde and/or acetic acid (partially oxidized reaction products), but it is difficult to discern between the carbonyl groups from acetaldehyde and acetic acid because the bands appears at very close frequencies (1713 and 1715 cm^{-1} , respectively) in the spectra [24]. In addition, the band at

1280 cm^{-1} is attributed to the C–O stretching vibrations in acetic acid and the bands at 1391 and 1370 cm^{-1} are associated to O–H deformation vibrations and CH_3 symmetric deformation in acetaldehyde, respectively [25]. Finally, it can be observed a signal at ca. 1110 cm^{-1} related to perchloric acid solution, use as base electrolyte, and acetaldehyde. It is difficult to distinguish between acetic acid and acetaldehyde signals because all of them appear at similar wavelengths. Only the band at 1280 cm^{-1} , related to acetic acid formation, is clearly separated from the others. The differences in the CO, CO_2 , CH_3COOH band intensities at different potentials can be better analyzed as plotted in Figure 9. The relative band intensity of CO_{ad} was found to be significantly lower during the EOR on Pt/CNF catalyst than on Pt/Vulcan catalysts, especially at low EOR overpotential. Whereas, the band intensity ascribed to acetic acid (CH_3COOH) was slightly higher on the Pt/CNF catalyst. These results suggest that the EOR via acetic acid formation is more favored when CNF is the carbon support, which is in total agreement with DEMS experiments. The very low CO_{ad} produced on Pt/CNF may explain the highest current densities for the EOR found (Figure 6), since a higher amount of Pt active sites is available during the EOR. Additionally, the eventual low amounts of CO_{ad} formed on the Pt/CNF catalyst are more easily oxidized at lower overpotentials, as seen previously (Section 3.2).

4. Conclusions

In the present work we have evaluated the influence of the carbonaceous support in the electro-activity of Pt/C catalysts toward CO and ethanol oxidation reactions. The carbon supports studied were in-house synthesized carbon nanofibers, Vulcan and functionalized Vulcan, i.e. with higher amount of surface oxygenated groups. All Pt/C

catalysts were synthesized via the formic acid method, obtaining quite similar structural characteristics as particle size or crystal phases.

The CO stripping voltammograms for Pt/Vulcan and Pt/Vulcan NSTa0.5 showed one single peak at 0.77 V vs. RHE, while Pt/CNF showed two oxidation peaks, the main one taking place at 0.75 V vs. RHE and the second one at more negative potential (0.66 V vs. RHE), suggesting a higher CO tolerance of the catalysts supported on CNF compared to those on Vulcan (either functionalized or not).

The EOR cyclic voltammograms and current transient curves for the three catalysts evidenced the following order of activity: Pt/Vulcan < Pt/Vulcan NSTa0.5 < Pt/CNF.

In situ spectroelectrochemical techniques such as FTIR and DEMS were employed in order to identify adsorbed reaction intermediates and products and volatile reaction products, respectively. Both *in situ* spectroscopy results suggest that the higher CO tolerance of Pt supported on CNF, allowing a higher density of available Pt active sites for the EOR, resulting in higher current densities. However, a higher selectivity to acetic acid was favored on Pt/CNF, thus, the highest current density for Pt/CNF catalyst results from higher amount of C₂ products obtained during the incomplete EOR.

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Tables

Table 1: Composition and structural characteristics obtained from EDX (*) and XRD ()**

Catalyst	*% Metal content wt.	**Cristallite size (nm)	**Lattice Parameter (Å)
Pt/Vulcan XC-72R	19	3.5	3.92
Pt/Vulcan NSTa0.5	18.5	3.8	3.92
Pt/CNF	19	5.3	3.92

Table 2: Weight percentages of the different Pt species and carbon extracted from XPS experiments

Catalyst	% Pt (IV)	% Pt (II)	% Pt (0)	% C1s
Pt/Vulcan XC-72R	9	19	72	75
Pt/Vulcan NSTa0.5	2	17	81	73
Pt/CNF	6	31	63	57

Table 3: Calculated average efficiency to CO₂.

Catalyst	CO ₂ conversion efficiency (%)
Pt/Vulcan XC-72R	2
Pt/Vulcan NSTa0.5	1.5
Pt/CNF	0.9

Figures

Figure 1

Figure 2

Figure 3.

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure captions

Figure 1. X-ray diffractograms of Pt/C catalysts.

Figure 2. Pt 4f XP spectra of Pt/C catalysts.

Figure 3. Simultaneously recorded CV and MSCVs for $m/z = 22$, $m/z = 44$ for CO stripping on (a) Pt/CNF, (b) Pt/Vulcan NSTa0.5 and (c) Pt/Vulcan XC-72R, in 0.5 M H_2SO_4 at room temperature

Figure 4. In situ FTIR spectra recorded during CO stripping on the Pt/CNF, Pt/Vulcan NSTa0.5 and Pt/Vulcan XC-72R catalysts in 0.5 M HClO_4 .

Figure 5. Comparative of CO_2 (2342 cm^{-1}) band intensities on the Pt/CNF, Pt/Vulcan NSTa0.5 and Pt/Vulcan XC-72R catalysts at different potentials during CO stripping.

Figure 6. Cyclic Voltammograms a) and current-transient curves b) recorded during ethanol oxidation reaction on Pt/CNF, Pt/Vulcan NSTa0.5 and Pt/Vulcan XC-72R in 1 M $\text{CH}_3\text{CH}_2\text{OH} + 0.5\text{ M H}_2\text{SO}_4$ at room temperature.

Figure 7. Simultaneously recorded CVs and MSCVs for $m/z = 22$, $m/z = 29$, $m/z = 44$, $m/z = 15$ for the oxidation of ethanol on Pt/CNF, Pt/Vulcan NSTa0.5 and Pt/Vulcan XC-72R in 0.05 M $\text{CH}_3\text{CH}_2\text{OH}$ and $m/z = 61$ in 1 M $\text{CH}_3\text{CH}_2\text{OH} + 0.5\text{ M H}_2\text{SO}_4$ at room temperature.

Figure 8. In situ FTIR spectra recorded during ethanol electrooxidation on Pt/CNF, Pt/Vulcan NSTa0.5 and Pt/Vulcan XC-72R in 1 M $\text{CH}_3\text{CH}_2\text{OH} + 0.5\text{ M HClO}_4$.

Figure 9. CO (2029 cm^{-1}), CO_2 (2342 cm^{-1}) and CH_3COOH (1280 cm^{-1}) band intensities on Pt/CNF, Pt/Vulcan NSTa0.5 and Pt/Vulcan XC-72R at different potentials.