Titanium carbonitride–graphene composites assembled with organic linkers as electrocatalytic supports for methanol oxidation reaction

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Abstract

In the present work, the effect of different composites as electrocatalytic supports for the methanol oxidation reaction is evaluated. Two different TiCN-rGO composites, using organic compounds as linkers were synthesized. Subsequently, platinum was incorporated in the form of nanoparticles, and the electrocatalysts were characterized and compared with similar nanoparticles supported on TiCN. The electrocatalysts were characterized by XPS, TEM, XRD, Raman and FTIR spectroscopies and ICP-MS and the catalytic performance toward CO_{ads} and methanol oxidations was evaluated. Results showed that the platinum nanoparticles were preferentially deposited on top of the TiCN particles rather than on the reduced graphene oxide, which allowed the nanoparticles to benefit from the TiCN electronic promoting effect. In addition, the presence of reduced graphene oxide contributes on the improvement of the morphological properties of the electrocatalyst, reducing the agglomeration degree of the particles and considerably enhancing the catalytic mass activities.

Keywords: methanol oxidation reaction, graphene composites, electrocatalytic supports, TiCN, platinum

Introduction

The direct methanol fuel cell (DMFC) is a promising portable electronic device, which enables the direct conversion of the chemical energy stored in liquid methanol fuel to electrical energy, with water and carbon dioxide as by-products. Therefore, DMFCs do not require the electrical charging process in comparison with traditional secondary batteries [1-3]. Compared to the well-known hydrogen fuelled proton exchange membrane fuel cells (PEMFCs), DMFCs use a less expensive fuel (per unit energy) and that provides higher volumetric and gravimetric energy density compared to compressed hydrogen (at 1000 bar) [1].

In the DMFC, a methanol/water mixture is directly fed to the anode in which the electrocatalytic process can be achieved at temperature lower than 100°C and atmospheric pressure. However, the methanol electrooxidation is a six electron pathway, involving different steps and intermediate species such as CO, formaldehyde, and/or formic acid [4, 5]. The formation of these compounds is responsible for the sluggish kinetics of the methanol oxidation reaction (MOR) and for the low efficiencies, as the formation of final products different than CO₂ involves the exchange of a lower number of electrons [6]. Since the catalyst determines the overall reaction efficiency, durability and cost, the development of suitable electrocatalyst materials plays a vital role for DMFCs.

Commonly, Pt-based nanoparticles are used as electrocatalysts for MOR, as platinum is a highly active material for these reaction [7-10]. A remarkable approach to reduce the cost and enhance the catalytic activity of platinum is through the catalyst support, which enables to produce nanoparticulated and highly dispersed electrocatalysts [11-13]. The nature of the support can modify the properties of the platinum nanoparticles, leading to a modification of the number and nature of active sites, which could alter significantly the electrocatalytic activity of the catalyst. The support can also provide synergetic effects, changing the electronic properties of the active sites, which affects the adsorption strength of molecules in the surface and consequently the reactivity [13]. Over the past decades, carbon materials have been widely used as electrodes in low temperature fuel cells, because they have extraordinary physical properties such as high surface areas and good electronic conductivity [14]. The major problem regarding the use of carbon materials, especially carbon blacks, as electrocatalyst supports is their low resistance to corrosion caused by electrochemical oxidation [15]. An alternative strategy is to use transition metal carbide and nitride materials [16-21]. Among them, titanium carbides and nitrides are well-known for its high melting point, high resistance to oxidation and corrosion, good thermal and electrical conductivity [22-25]. Previous studies of our team revealed a good performance of TiC, TiCN and TiN supported Pt nanoparticles for CO and methanol electrooxidation reactions in

acidic media [13, 24]. The electronic effect observed by the Ti-based supports led to a considerable enhancement of the CO tolerance respect to carbon-supported catalysts. Additionally, it was observed that for electrochemically surface oxidized TiC and TiCN supported platinum catalysts (1.0 V vs RHE), the activity toward methanol oxidation was several fold higher than for unmodified TiC and TiCN supported catalysts and even higher than that achieved by a commercial PtRu/C [24]. Nevertheless, the specific surface areas of these titanium carbides and carbonitrides are rather low, due to their large molecular weights [26, 27]. The last leads to low mass activity of the catalysts. In order to address this issue, new TiCN-graphene composites have been developed in this work. Graphene oxide (GO) with a layered structure and rich in functional surface groups is introduced to anchor the TiCN particles and increase the surface area of the hybrid material. The use of TiCN-graphene composites in the DMFC electrode offers important advantages. The graphene structure can provide interconnected electronically conductive pathways during fuel cell operation. They also possess a one dimensional anisotropic morphology that can result in enhanced electron transport properties for electrocatalyst materials and can serve to enhance mass transport properties electrode structures [28]. Moreover, TiCN can further provide a protective barrier in order to hinder the rates of carbon corrosion during fuel cell operation, and, as mentioned above, TiCN offers advantageous Pt-support interactions, including enhanced MOR activity along with improved CO tolerance [13, 24].

Herein, a series of TiCN-graphene composites are produced by intercalation of different organic linkers (ethylenediamine or poly(ethyleneimine)) in order to facilitate the interconnection between reduced graphene oxide and TiCN particles. After that, Pt catalysts are prepared by reducing Pt nanoparticles in the TiCN-reduced graphene oxide composites by ethylene glycol method (EG). The effect of organic linker in the preparation of the TiCN-reduced graphene oxide supports has been evaluated for the CO and methanol oxidation reaction in acidic media.

1. Experimental

Three different materials were used as electrocatalytic supports for platinum nanoparticles. Two of them were TiCN-reduced graphene oxide composites prepared in our laboratories using ethylenediamine or poly(ethyleneimine) as organic linkers, while the third one was commercially available TiCN, which has already been studied elsewhere [13], and that was used in this study as a reference.

1.1. Composite supports preparation

Two different TiCN-reduced graphene oxide composites were synthesized by a sol-gel method. Graphene oxide (GO, Sigma Aldrich) was suspended on water ($3 \text{ mg} \cdot \text{mL}^{-1}$) and the appropriate amounts of titanium carbonitride (TiCN, Sigma Aldrich, $\text{TiC}_{0.7}\text{N}_{0.3}$) and linker were added. The ratio TiCN:GO was kept at 10:1. Two different linkers were employed: ethylenediamine (EDA, Sigma Aldrich) and poly(ethyleneimine) (PEI, Sigma Aldrich, 50% solution in water) with a nominal percentage of 5 wt.% with respect to TiCN. The two composite precursors were properly mixed and afterwards, heated at 120°C for three hours. Finally, the two different composite samples were dried following a supercritical drying process, which was carried out in a homemade autoclave at controlled pressure and temperature. The composites were placed in the autoclave with absolute ethanol. The autoclave was sealed, and N_2 pumped in with the outlet was open for 15 min. The outlet and inlet valves were closed, and the temperature was raised from 25°C to 250°C by the heating system. The system was slowly depressurized when the pressure of the system exceeded 1100 psi. Finally, the temperature was maintained at 280°C for 2 h under N_2 after depressurization. GO is reduced after this supercritical drying process [29]. The prepared supports were labeled as TiCN-EDA and TiCN-PEI, indicating which linker was employed in each case.

1.2. Synthesis of the electrocatalysts

Three different platinum catalysts were synthesized following the ethylene glycol method [30]. The difference among the three catalysts was the support employed: the in-house synthesized TiCN-ED and TiCN-PEI composite supports and the commercially available TiCN. Ethylene glycol (>99%, Sigma–Aldrich) was used as solvent and reducing agent. Appropriate amounts of platinum precursor (99.99% PtCl_4 from Alfa Aesar) were employed to obtain a nominal metal loading of 20 wt.% on the catalyst support. The one-pot synthesis method consisted in the addition of the metal precursors previously dispersed in ethylene glycol into a suspension of the catalyst support in the same solvent. Then, the pH was adjusted to 11 and the temperature increased to 160°C under a N_2 flow. After 3 h, the pH was adjusted to 2 and the catalysts were washed with acetone and later rinsed with water and dried at 80°C . Finally, a thermal treatment was carried out under He flow (80 mL min^{-1}) during 1 h at 250°C . The three catalysts were labeled as Pt/TiCN, Pt/TiCN-EDA and Pt/TiCN-PEI.

1.3. Physicochemical characterization

The chemical composition of the catalysts was determined by an inductively coupled plasma optical emission spectrometry (ICP-MS). The samples were previously digested with a high pressure Multiwave 3000 Anton Paar working at 60 bar at 210 °C in a mixture of acids HNO₃, HCl, HF y H₃PO₄ (3:2:3:3 mL). The amounts of C, H and N were determined by a CHN elemental analysis on a LECO CHNS-932 equipment. X-ray diffractograms were obtained on a PANalytical X'Pert Pro X-ray diffractometer with a Cu K α source. Bragg's angles ranging from 4° to 90° were recorded at a scan rate of 0.02° per second and with an accumulation time of 500 s.

Thermogravimetric analyses (TGA) were performed in a Mettler Toledo TGA/SDTA 851e equipment, with a 1 μ g precision. Analysis were performed with 5 mg of the sample and a heating rate of 10°C·min⁻¹ and up to 1000°C in O₂. BET surface area determinations were performed with an ASAP 2420 Micromeritics analyser, and after degassing for 3 h at room temperature.

Transmission electron microscopy images were obtained from a HRTEM JEOL 2100F operating at 200 eV. Obtained images were used to evaluate the morphology and agglomeration degree, as well as to calculate the average nanoparticle sizes. For that purpose, the diameter of a minimum of 300 nanoparticles was determined.

X-ray photoelectron spectroscopy (XPS) data was obtained with a VG ESCALAB 200R spectrometer with a hemispherical electron analyzer, five channeltron detectors and a X-ray Mg K α (1253.6 eV) excitation source operating at 12 kV and 10 mA. The working pressure was always below 7·10⁻⁹ mbar. The powder samples were attached onto a Cu foil and were placed first in the pre-treatment chamber at room temperature for several hours before being transferred to the analysis chamber. The XPS data were signal averaged for enough number of scans to get a good signal/noise ratio, at a fixed pass energy of 50 eV. High-resolution spectra envelopes were obtained by curve fitting synthetic peak components using the software XPSpeak. The raw data were used with no preliminary smoothing. Symmetric Gaussian-Lorentzian product functions were used to approximate the line shapes of the fitting components. Binding energies were calibrated relative to the C 1s peak from the graphitic carbon at 284.6 eV.

Raman spectra were obtained with a Renishaw in Via Raman Microscope equipped with a 532 nm green laser and a 5 mW power, operating at 1% of the maximum power. The spectral resolution was around 1 cm⁻¹ and the spectra acquisition was recorded with 5 accumulations of 10 seconds each.

1.4. Electrochemical characterization

All measurements were carried out in a three-electrode cell at room temperature controlled by an Autolab PGSTAT302 potentiostat-galvanostat. A glassy carbon rod was used as counter electrode while a reversible hydrogen electrode (RHE) in the supporting electrolyte was used as reference. The working electrode was prepared by depositing 20 μL of catalytic ink onto a glassy carbon (area 0.28 cm^2). The catalytic ink was prepared by sonicating 2 mg of catalyst with 15 μL Nafion[®] (5%, Sigma Aldrich) and 500 μL of ultrapure water (MilliQ, Millipore). 0.5 M H_2SO_4 (EMSURE[®] ISO, Merck) was used as electrolyte while 2 M CH_3OH (EMSURE[®] ISO, Merck) + 0.5 M H_2SO_4 solution was used to study the MOR. N_2 (99.999%, Air Liquide) was employed to deoxygenate all solutions and CO (99.997%, Air Liquide) for CO stripping experiments. An electrochemical activation of the electrode was performed by potential cycling between 0.05 and 0.9 V vs RHE at a scan rate of 0.1 $\text{V}\cdot\text{s}^{-1}$ during 50 cycles. CO stripping experiments were recorded at 0.02 $\text{V}\cdot\text{s}^{-1}$ after bubbling CO through the cell for 10 min while keeping the electrode at 0.10 V, followed by N_2 purging during 30 min to completely remove the excess of CO. CO stripping voltammograms were recorded, by first scanning negatively until 0.05 V so that the entire hydrogen region was probed, and then scanning positively up to 0.9 V. Methanol cyclic voltammograms (CVs) were recorded between 0.05 and 0.9 V at a scan rate of 0.02 $\text{V}\cdot\text{s}^{-1}$, while current transients were obtained by jumping from a potential of 0.05 V to a final potential of 0.65 V. The accelerated stability test (AST) was performed by cycling the catalysts between 0.05-1.0 V at 0.5 $\text{V}\cdot\text{s}^{-1}$ for 10000 cycles. After 1000, 2000, 3000, 5000, 7000 and 10000 cycles, a blank voltammogram at 0.02 $\text{V}\cdot\text{s}^{-1}$ was recorded.

2. Results and discussion

2.1. Structural characterization

TiCN-based supports

Two different TiCN-reduced graphene oxide composites were synthesized. The addition of organic linkers was necessary in order to achieve an appropriate interaction between the two materials. For this reason, ethylenediamine (EDA) and poly(ethyleneimine) (PEI) were used as linkers. The in-house synthesized composite TiCN-reduced graphene oxide supports were characterized before the addition of the platinum nanoparticles. The elemental analysis was performed by ICP-MS (for Ti) and a C,H,N analysis. The results obtained at both techniques are displayed at Table 1. In addition, an estimation of the weight percentage of TiCN, reduced graphene oxide and linker was performed. This estimation was done considering that all the

graphene oxide was reduced to graphene and that the organic linker remained unaltered. Thus, it must be taken carefully. The greater decrease in the percentage of PEI (3.2 wt%) and EDA (1.1 wt.%) with respect to the nominal percentage (5 wt. %) may be due to a loss by evaporation or decomposition of part of the linkers during composite formation. Actually, while the elemental analysis seems accurate for the TiCN-EDA support, it is evident that the TiCN-PEI sample contains an additional element, as the total composition is far from 100%. This extra element may correspond to oxygen belonging to unreduced graphene oxide.

Table 1. Elemental analysis of supports

		TiCN	TiCN-EDA	TiCN-PEI	Stoichiometry for $\text{TiC}_{0.7}\text{N}_{0.3}$
Elemental analysis results	C (%)	14.00	17.74	17.76	13.89
	N (%)	6.95	7.03	6.89	6.95
	H (%)	0.24	0.26	0.30	-
	Ti (%)	78.9	74.2	66.9	79.16
	Total (%)	100.09	99.23	91.85	100.00
Estimated composition	TiCN (%)	100.0	93.7	84.6	-
	Reduced graphene oxide (%)	-	4.3	4.3	-
	Linker (%)	-	1.1	3.2	-

The in-house prepared composites were also analyzed by TEM. Figure 1 shows TEM micrographs of the two composites compared to the commercial TiCN sample. It should be noted that the images of TiCN-EDA and TiCN-PEI composites are not completely representative of the samples, as two different morphologies were detected. In these two materials, some locations analyzed by TEM were similar to TiCN, i.e. with the presence of agglomerated particles, and in other spots, TiCN particles with reduced graphene oxide sheets were observed (as shown in Figure 1A and 1B). The last is expected, since these composites only contain approximately 4 wt.% of reduced graphene oxide (Table 1). According to the TEM images of the three supports with the same magnification (Figure 1A), the presence of reduced graphene oxide sheets causes

a reduction of the agglomeration degree of the TiCN particles. Furthermore, an increase of the BET surface area was detected for the composites, shifting from 20 m²/g of TiCN to 34 m²/g of TiCN-PEI and 49 m²/g of TiCN-EDA. Having in mind that the amount of reduced graphene oxide in both samples is the same, it seems that the nature of the organic linker has a crucial effect on the interaction between reduced graphene oxide and TiCN. EDA appears as considerably better in order to achieve a good dispersion of the TiCN particles on top of the reduced graphene oxide sheets. Thus, it can be concluded that the presence of reduced graphene oxide sheets and organic linkers allow a better dispersion and accessibility of the TiCN particles.

Figure 1. TEM images of TiCN, TiCN-EDA and TiCN-PEI supports with the same magnification (A) and TEM images of TiCN-EDA and TiCN-PEI with lower magnification (B)

The three different materials used as supports were also analyzed by XPS in order to evaluate the chemical and electronic state of its surface. The Ti 2p core-level spectrum of each material is shown in Figure 2. The XPS analysis of the supports reveals that the interaction between reduced graphene oxide and TiCN does not cause a major modification of the carbonitride material surface oxidation or electronic state, as any modification on the relative intensities of the different

contributions was observed, as well as any shift of the peaks. The Ti 2p region of TiCN is characterized for the presence of contributions corresponding to reduced TiCN (blue line in Figure 2), partially oxidized oxycarbonitride species (purple line in Figure 2) and completely oxidized TiO_2 (green contribution at Figure 2), as described elsewhere [31]. In this case, the relative contributions is kept unaltered at the three different materials: the contribution of reduced TiCN corresponds to 54% for the TiCN support, 52% for TiCN-EDA and 51% for TiCN-PEI, the contribution of oxycarbonitride is 24 % for the TiCN support and 26% for both composites, while the contribution of TiO_2 accounts for 22% for TiCN and TiCN-EDA and 23% for the TiCN-PEI support. In addition the maximum of the peaks and the position of each contribution in the fittings appear at the exact same binding energy in all three cases. FTIR and Raman analysis (supporting information, Figures S1 and S2) also do not show any difference among the three materials. In both cases, only the characteristic bands of the TiCN are detected. Thus, it can be concluded that the interaction between TiCN, reduced graphene oxide and the organic linkers is basically morphological and it does not suppose a major electronic exchange or modification.

Figure 2. Ti 2p core-level of the supports

Figure 3 shows the TGA and DTG obtained for the three supports in oxygen. Similar behavior for the TiCN-EDA and TiCN-PEI composites can be observed, but with some differences with

respect to the TiCN. The TiCN presents a minor weight loss in the range of 100-150°C due to the evaporation of the adsorbed moisture, which is not observed in TiCN-reduced graphene oxide composites. The supercritical drying treatment removes the water retained in these composites. At a temperature above 400 °C, a manifest weight increase is observed in all supports, corresponding to the oxidation of TiCN to TiO₂. It should be noted that the oxidation process to TiO₂ of the composites takes place at slightly higher temperatures than for TiCN. This would indicate that TiCN is stabilized when is in contact with the reduced graphene oxide and linkers. Moreover, the composites show two slight weight losses around 270-360 °C and 575-620 °C, which are not observed for the TiCN. The first one could be attributed to the decomposition of the linkers [32]. The second weight loss from 575 °C corresponds to the complete oxidation of graphene [33].

Figure 3. Thermogravimetric analyses (A) and DTG (B) of the supports in oxygen flow

Pt/TiCN-based electrocatalysts

Once the three different materials to be used as electrocatalytic supports were characterized, the platinum nanoparticles were incorporated following the ethylene glycol synthesis method. The experimental Pt-loadings determined by ICP-OES are shown in Table 2. Platinum nanoparticles were successfully deposited on the three different supports, even though the Pt loading on the TiCN-reduced graphene oxide composites are slightly lower than the theoretically expected (20 wt%).

The TEM images of the electrocatalysts are shown in Figure 4A. It shows images of the three catalysts under the same magnification. It is possible to observe that the agglomeration degree of the platinum nanoparticles seems to decrease when the composite supports are employed than

for Pt/TiCN. Like in the case of the supports, two different morphologies were observed for the Pt/TiCN-EDA and Pt/TiCN-PEI: in some spots only platinum nanoparticles deposited on TiCN were observed, while in other spots some reduced graphene oxide sheets were also present (representative images in Figure 4B). In this last case, it was always detected that the platinum nanoparticles were deposited on top of the TiCN particles, and hardly ever on the reduced graphene oxide layers. The last may be due to the stronger interaction of the platinum nanoparticles with the TiCN support rather than with carbon. That was experimentally corroborated in our previous works by means of XPS and *in situ* FTIRs measurements [13, 31]. The preferential deposition of the platinum nanoparticles on top of the TiCN is of great importance, as it is known that the TiCN support exerts an important promotion effect on the methanol oxidation reaction [24]. From the analysis of several TEM images, the average particle size was calculated for each catalyst, and the values are summarized at Table 2. The particle sizes of the different catalysts are similar, which makes sense having in mind that the platinum nanoparticles are deposited on top of the TiCN.

Figure 4. TEM images of the Pt/TiCN-based electrocatalysts, Pt/TiCN-EDA and Pt/TiCN-PEI electrocatalysts with the same magnification (A), and TEM images of Pt/TiCN-EDA and Pt/TiCN-PEI with lower magnification

The X-ray diffraction profiles of the catalysts were also recorded, and are collected in the supporting information (S3). In all of them, the diffraction peaks are analogous and attributed to fcc Pt (JPCDS 00-004-0802) and $\text{TiC}_{0.7}\text{N}_{0.3}$ (JPCDS 00-042-1489) crystalline phases. As expected, no difference is observed when reduced graphene oxide and the organic linker are incorporated. The width of the platinum diffraction of the three samples confirms that the nanoparticles sizes are similar in all the catalysts.

The XPS analyses of Pt 4f core-levels are shown in Figure 5, while the binding energies are summarized at Table 2. The Pt 4f signal could be resolved into three doublets in all electrocatalysts. The most intense Pt 4f_{7/2} component at lower binding energy is attributed to metallic Pt. The second doublet can be assigned to Pt (II) in PtO and Pt(OH)₂ like species, while the third doublet at higher binding energy corresponds to the higher oxidation state of Pt(IV). According to data collected in Table 2, the platinum contribution appears at the same BE in the three cases. Previously, our team reported a strong electronic effect between platinum NP and the TiCN support [13], which caused a large shift of the XPS peak comparing to Pt/C catalyst. Then, the XPS results of the composites reveal that this strong interaction Pt-TiCN is maintained even with the incorporation of reduced graphene oxide and the organic linker, which also do not modify the electronic or chemical structure of the platinum nanoparticles. The last is in agreement with the TEM images, where it was observed that almost the total amount of the platinum nanoparticles are on top of the TiCN and thus, there is no interaction between these nanoparticles and the reduced graphene oxide. Regarding the Ti 2p region, in this case, some differences are observed among the different catalysts (Table 2). Even though the three different supports had a comparable titanium surface chemical state before the incorporation of the platinum nanoparticles (Figure 2), after the ethylene glycol synthesis, the catalysts containing reduced graphene oxide and organic linkers possess a slightly higher amount of more reduced titanium species (more TiCN and less TiO₂, Table 2) than the catalyst supported on bare TiCN. Actually, in all three cases the surface appears to possess a higher degree of oxidized species than before the incorporation of platinum. This slightly higher amount of oxidized titanium species for the Pt/TiCN catalysts is in complete agreement with the TGA results presented in Figure 3, where the TiCN support was easily oxidized (lower temperature) than the TiCN-PEI and TiCN-EDA supports.

Summarizing, the structural characterization shows that the three synthesized electrocatalysts possess similar morphological, chemical and electronic properties. The presence of reduced graphene oxide and the organic linkers seems to only allow a better dispersion and accessibility

of the TiCN particles, while the electronic and chemical properties of both the TiCN and the platinum nanoparticles are not significantly altered. Finally, the platinum nanoparticles are preferentially deposited on top of the TiCN particles due to the strong metal support interaction between them.

Table 2. Physicochemical characterization of the electrocatalysts

			Pt/TiCN	Pt/TiCN-EDA	Pt/TiCN-PEI
ICP-MS		% _w of Pt	19.2	17.0	16.1
TEM		Particle size (nm)	4.2±1.0	4.3±1.4	4.4±1.3
XPS	Pt 4f	Pt (0)	71.2 eV (63%)	71.2 eV (64%)	71.1 eV (64%)
		Pt (II)	72.8 eV (26%)	72.8 eV (26%)	72.7 eV (26 %)
		Pt (IV)	74.4 eV (11%)	74.6 eV (10%)	74.6 eV (10%)
	Ti 2p	TiCN	455.2 eV (32%)	455.2 eV (39%)	455.1 eV (41%)
		oxycarbonitrides	456.8 eV (20%)	456.8 eV (18%)	456.9 eV (18%)
		TiO ₂	458.5 eV (48%)	458.4 eV (43%)	458.4 eV (41%)

Figure 5. Pt4f core-level spectra of the electrocatalysts

2.2. Electrochemical characterization

The electrocatalysts were tested toward the oxidations of CO_{ads} and methanol in a three electrodes cell. Carbon monoxide is a reaction intermediate of the methanol oxidation, but it also behaves as a catalyst poison due to its strong adsorption on platinum surfaces. Therefore, during the methanol oxidation, the catalyst surfaces may become blocked with this intermediate, hindering the reaction kinetics. For this reason, it becomes necessary to study and understand the CO_{ads} oxidation reaction on the catalysts to be used for the methanol oxidation reaction. Figure 6 shows the CO stripping results for the three different catalysts. A monolayer of carbon monoxide was adsorbed on the catalysts and subsequently oxidized (colored lines). The figures also show the following voltammogram cycle (black lines), recorded on the freshly catalyst surfaces obtained after the oxidation. During the first cycle, a multiple oxidation peak was detected for all the catalysts, corresponding to the oxidation of the adsorbed CO monolayer. In the subsequent cycle, the typical profile of platinum nanoparticles was recorded. The presence of two main contributions on the CO_{ads} oxidation profile is commonly attributed to the presence of different active sites on the platinum surface or the different adsorption geometries of the carbon monoxide molecule (linear, bridge...). Extensive studies with platinum single crystals demonstrated that the different surface orientations and atomic coordination (atoms at terraces, steps...) lead to a modification of the CO and water adsorption strengths and thus, to the oxidation at a different potential. For nanoparticles in acid media, commonly the adsorbed carbon monoxide molecules diffuse through the platinum surface to the most reactive active sites giving rise to a single oxidation peak [34]. The presence of several contributions is only detected when the different active sites are not interconnected. However the display of two oxidation contributions is typical of platinum catalysts supported on TiCN, and in our previous studies, it was proposed to be due to the oxidation at two different active sites: the contribution at higher potentials corresponding to the oxidation of CO adsorbed on top of the platinum nanoparticles, while the contribution at lower potentials, corresponding to the oxidation of carbon monoxide adsorbed close to the platinum-titanium interface, where titanium oxide species act as promoters for the reaction [24]. Our experiments showed that an increase of the oxidation degree of the TiCN surface led to an increase of the CO_{ads} oxidation peak at low potential. Having a closer look at the relative intensities of the two contributions present at Figure 6, it is possible to find a correlation with the amount of surface titanium oxide detected by XPS; Pt/TiCN catalyst has a higher amount of TiO_2 surface species, and thus, develops a more intense oxidation contribution at lower potentials, while for the Pt/TiCN-PEI catalyst, which has more reduced titanium surface

species (according to the XPS results), this contribution is less intense. Regarding the Pt/TiCN-EDA electrocatalyst, its main oxidation peak appears at a slightly higher potential than for Pt/TiCN. The last may be due to a small blocking effect of the organic linker residues. However, both catalysts supported on TiCN-reduced graphene oxide composites maintain the promoting effect of the TiCN catalyst support, as the onset potential for the CO_{ads} oxidation is, in all cases similar and considerably lower than those reported for Pt/C catalysts synthesized following the same method [13].

The current densities in Figure 6 were normalized by the electrochemical surface areas (ECSA), the accessible platinum area. The ECSA values were calculated from the integration of the CO_{ads} stripping voltammograms. The values obtained were 1.9 cm^2 for the Pt/TiCN electrocatalyst, 3.3 cm^2 for Pt/TiCN-PEI and 5.3 cm^2 for Pt/TiCN-EDA. The different ECSA values obtained for catalysts with almost the same platinum nanoparticles sizes and loading clearly indicates that the noble metal nanoparticles do not have the same accessibility in all the cases. For the Pt/TiCN electrocatalyst, the ECSA is considerably lower, pointing out that the platinum nanoparticles are highly agglomerated and non-accessible for the probe molecule (CO). The last is in agreement with high agglomeration degree of the platinum nanoparticles supported on TiCN observed by TEM. On the other hand for the two catalysts which incorporate reduced graphene oxide and organic linkers, and especially for Pt/TiCN-EDA, the ECSA values are considerably higher, indicating that the platinum nanoparticles are more accessible, and so, the noble metal is better exploited. It is also important to remark that, as expected, there is a direct relationship between the BET surface area of the supports and the ECSA of the catalysts once the platinum is incorporated.

Figure 6. CO stripping voltammograms of the electrocatalysts recorded in 0.5 M H₂SO₄. $E_{ad} = 0.1$ V, scan rate = $0.02 \cdot V \cdot s^{-1}$.

After observing that the promoting effect of TiCN is still present on the catalysts supported on the composites, the methanol oxidation reaction was studied. The cycling voltammograms recorded in an electrolyte containing methanol in 2M concentration are displayed in Figure 7. At the left panel, the signals are normalized by the ECSA values in order to compare the intrinsic activity of the catalyst (specific activity; activity/active site), while in the right panel, the same signal is displayed after a normalization by the total platinum amount on each catalyst (mass activity). Exploring first the left panel, it can be observed that the onset potential is identical in the three catalysts, and the current densities obtained are also quite similar, especially at lower overpotentials. The only difference comes from the Pt/TiCN-EDA catalysts, which seems to present a small kinetic impediment. These observations corroborate that the promoting effect of the TiCN support is maintained in the composites. However, when the results are normalized by the mass of noble metal (right panel), the catalyst supported on the composites become considerably more active than the supported on TiCN.

Figure 7. Methanol oxidation cyclic voltammeteries of the electrocatalysts recorded in 0.5 M H_2SO_4 . Scan rate = $0.02 \text{ V}\cdot\text{s}^{-1}$.

This effect is even more visible under steady-state conditions, corresponding to the current transients recorded at 0.65V (Figure 8). In this case, the current developed by the Pt/TiCN-EDA catalysts is more than three times higher than that of Pt/TiCN. The differences on the mass activity of the three catalysts are clearly related with the different platinum ECSAs developed depending on the catalytic support. The last indicates that even though the three catalysts contain a similar amount of platinum, the accessibility of the noble metal is quite different. This seems to be because the reduced graphene oxide contributes on reducing the agglomeration degree and improves the accessibility of both the TiCN particles and the platinum nanoparticles. The last was already observed during the TEM analysis. As a consequence, the mass activities of the catalysts supported on composite supports are considerably higher than the catalysts supported on bare TiCN. Thus, the reduced graphene oxide sheets are performing a beneficial morphological effect but they do not suppress the promoting electronic effect performed by the TiCN particles. As a consequence, the catalysts benefit both from the morphology of the reduced graphene oxide and the promotion effect of the TiCN particles, being able to surpass one of the main drawbacks of the transition metal carbides and nitrides supported electrocatalysts: their low surface areas.

Figure 8. Current transients corresponding to the oxidation of 2M methanol on 0.5M H₂SO₄ E₀=0.05 V. E_{final}=0.65 V.

Finally, the catalysts were subjected to an accelerated stability test, consisting of 10000 cycles between 0.05 and 1 V at 0.5 V·s⁻¹. After 1000, 2000, 3000, 5000, 7000 and 10000 cycles, the ECSA value was reevaluated by recording a blank voltammogram at 0.02 V·s⁻¹. The evolution of the ECSA of the three catalysts, expressed as the remaining % of initial ECSA is displayed at Figure 9. The results suggest that the catalyst supported on composites, and especially Pt/TiCN-EDA, are more stable than the Pt/TiCN catalyst. The last may be due to the improved stability of TiCN in the presence of reduced graphene oxide and the organic linkers, as was detected by TGA.

Figure 9. Evolution of the electrocatalysts ECSAs during an accelerated stability test consisting of a potential cycling between 0.05 and 1.0 V.

Summarizing, the mass activity and stability of a Pt/TiCN was improved by mixing the TiCN particles with small amounts of reduced graphene oxide in the presence of organic linkers. The promoting effect of TiCN remains, while the presence of reduced graphene oxide sheets reduces the agglomeration degree and thus, considerably improves mass activities. The promising results presented in this article, are a first approach on the preparation of TiCN-rGO-organic linker supported catalysts. A further exploration of new organic linkers in order to find those that can favor a good dispersion of the TiCN particles without compromising the electronic conductivity as well as an optimization of the amount of reduced graphene oxide incorporated in the composites may lead to a significant enhancement of the TiCN supported catalyst's mass activities.

Conclusions

In the present work, a new strategy was implemented in order to overcome the main drawback of the transition metal carbides and nitrides based electrocatalytic supports; its low surface area. Herein, two different composites were synthesized, made of TiCN, reduced graphene oxide and an organic compound (ethylenediamine or poly(ethyleneimine), respectively), which were used as linkers in order to improve the interaction between the other two. The characterization of these composites revealed that the synthesis did not affect the main chemical and physical properties of the TiCN particles compared to the bare TiCN. Only a slightly shift of the oxidation temperature to higher values was detected during the TG analysis. However, the presence of reduced graphene oxide considerably increased the BET surface area of the material, indicating that the TiCN particles were less agglomerated in the composites. It was later observed that the incorporated platinum nanoparticles laid almost exclusively on top of the TiCN particles rather than on the reduced graphene oxide sheets, which helped on keeping the electronic interaction observed between the TiCN particles and the platinum nanoparticles. Therefore, the specific activity of the two composite supported electrocatalysts was almost identical to that of the Pt/TiCN catalyst, both for the CO_{ads} and methanol oxidation reactions. However, the mass activity was considerably improved on the composite-supported catalysts, due to the lower agglomeration degree of the particles achieved thanks to the presence of the reduced graphene oxide sheets. Also the stability of the new electrocatalysts was demonstrated to be superior to Pt/TiCN. Both effects were more distinct for the Pt/TiCN-EDA catalyst.

Overall, the results presented in this work introduce a new strategy in order to improve the performance of TiCN as electrocatalytic support. The results clearly suggest that it is possible to take advantage of the promoting effect of transition metal carbides and nitrides supports while

achieving a much better morphology of the catalyst by introducing only small amounts of reduced graphene oxide. It is expected that further optimization of the amount of rGO and the organic linker nature may lead to even higher mass activity improvements.

Acknowledgements

Authors acknowledge financial support given by Spanish Ministry of Science, Innovation and Universities, through project ENE2017-83976-C2-1-R (co-founded by FEDER), Spanish National Research Council (CSIC) through project i-LINK1106 and Aragon Gouverment through Fuel Conversion Group (co-founded by FEDER).

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