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Titanium Carbide and Carbonitride Electrocatalyst Supports: Modifying Pt-Ti Interface Properties by Electrochemical Potential Cycling

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Experimental section

Pt nanoparticles (15 wt.%) supported on carbon black (C), TiC, TiCN and TiN were synthesized following the ethylene glycol method [1]. Carbon black (Vulcan XC-72R; BET surface area: 230 $m^2 \cdot g^{-1}$) from Cabot Corporation, and Ti-based materials (TiC, BET surface area: 23 $m^2 \cdot g^{-1}$; TiCN (7:3), BET surface area: 22 $m^2 \cdot g^{-1}$ and TiN, BET surface area: 5 $m^2 \cdot g^{-1}$) from Sigma-Aldrich were used as catalyst supports. The details of the synthesis process and the equipment used for the physicochemical characterization are described elsewhere [2].

All the electrochemical experiments were made in a three-electrode cell controlled by an Autolab PGSTAT302N potentiostat-galvanostat.

20 µL of a catalytic ink (dispersion of 4 $mg \cdot mL^{-1}$ of catalyst and 30 $\mu L \cdot mL^{-1}$ of 5 wt.%, Nafion® solution, Sigma Aldrich) where dried onto a glassy carbon electrode (0.28 cm^2) as working electrode. A carbon rod was used as counter electrode and a reversible hydrogen electrode (RHE) in the supporting electrolyte as reference.

CO and methanol electrooxidation reactions were studied by cyclic voltammetry and chronoamperometry by two different approaches: each catalyst was activated by potentiodynamic sweeps (50 cycles) between 0.05 and (i) 0.9 or (ii) 1.0 V at 100 mVs^{-1} in 0.5 M H_2SO_4 (Merck, p.a. in MilliQ water, Millipore). Subsequently, CO stripping experiments were performed in the same potential range after bubbling CO (99.997%, Air Liquide) in the electrolyte for 10 min, followed by electrolyte exchange and N_2 (99.99%, Air Liquide) purging for 30 min at controlled working potential of 0.1 V. After that, methanol electrooxidation reaction (2M CH_3OH, Scharlau, HPLC grade in H_2SO_4 0.5M) was studied by cyclic voltammetry in the same potential range, and subsequently current transients were recorded at 0.55 V for 400 seconds.

CO stripping experiments were used to study the CO tolerance and to obtain the electrochemical surface area (ECSA) that is used for current normalization on Fig. 1 and 3. The ECSA of the catalyst is calculated from the Columbic charge Q_{co} obtained from the CV experiment and the charge required to oxidize a monolayer of CO on Pt or PtRu (Q_{COref} = 420 µC/cm^2),

$$ECSA\ (cm^2) = \frac{Q_{CO}}{Q_{COref}}$$

In Fig. 4, the noble metal loading in the electrode was also taken into account. In this case the normalization factor was obtained from:

$$ECSA^*\ (cm^2 \cdot g^{-1}) = \frac{Q_{CO}}{Q_{COref} M_{Pt+Ru}}$$

where M_{Pt+Ru} corresponds to the Pt + Ru content or loading in the electrode (g of Pt +Ru).

In-situ Fourier Transform Infrared Spectroscopy (FTIRS) studies were performed with a NICOLET 6700 FTIR spectrometer equipped with a MCT detector and fitted with a PIKE Technologies VeeMAX II total reflection spectroscopic accessory. A poly (methyl methacrylate) cell with a 60º CaF_2 prism at its bottom was coupled to the spectrometer with an external reflection configuration. FTIRS spectra were acquired from the average of 32 spectra with a resolution of 4 cm^{-1}, applying 0.1 V single potential steps from a reference potential (E_o=0.1V) and up to 1.0 V. The reflectance ratio R/R_o was calculated. In this way, positive and negative bands represent loss and formation of species, respectively. The same electrodes as in the rest of the electrochemical measurements were used, except for the working electrode, which in this case was a gold disk (0.79cm^2) with the catalytic ink dried on it.

Results

The details of the synthesis process and the results of the characterization of the catalysts are described elsewhere [2]. Briefly, XRD showed high crystalline cubic structure for TiC, TiCN and TiN. XPS demonstrated that the interaction between titanium-based supports and platinum nanoparticles was high, resulting in a negative charge transfer from the support to the platinum. TEM images showed that the size of platinum particles was similar in all catalysts (Pt/C: 2.8±1.0 nm, Pt/TiC: 3.4±1.0 nm, Pt/TiCN: 4.6±1.5 nm, Pt/TiN: 4.3±1.1 nm) being slightly higher for those containing titanium-based supports (Fig. 1S). The catalyst support also affected the platinum agglomeration degree and number of low coordinated sites, which in turn affect the profiles of the blank, CO stripping and methanol oxidation voltammograms. Pt nanoparticles supported on titanium-based materials, and especially those containing nitrogen, presented a high density of low coordination sites with higher activity toward CO and methanol electrooxidation reactions.

Potentiodynamic electrooxidation of methanol are represented in Fig. 2S. The top panels show the voltammograms of the four catalysts after being activated up to 0.9 V while the bottom panels show the results for the catalysts activated up to 1.0 V. Positive going scans are used to compare the catalytic activity towards methanol oxidation for all catalysts. As in the case of CO stripping, Pt/C and Pt/TiN develop similar performance at both activation procedures, while Pt/TiC and Pt/TiCN enhance their activity when are activated up to 1.0 V. The latter is better observed in Table 1, in which the current densities at 0.7 V during the positive going scan are depicted.

Current transients normalized by the ECSA are depicted in Fig. 3S, in which is evident the catalytic activity change with the procedure achieved, i.e. activating up to 0.9 or 1.0 V. Catalytic activity of Pt/TiCN and Pt/TiC increase 1.5 and 5-fold when are activated up to 1.0 V. On the other hand, Pt/C and Pt/TiN activities are quite similar or decrease by the activation procedure. The last indicates that oxygenated species formed in the surface of TiC and TiCN supports at higher potentials of 0.9 V are acting as promoters for the CO and methanol electrooxidation reactions.

References

[1] C. Bock, C. Paquet, M. Couillard, G. A. Botton, B. R. MacDougall, *Journal of the American Chemical Society* **2004**, *126*, 8028-8037.

[2] M. Roca-Ayats, G. García, J. L. Galante, M. A. Peña, M. V. Martínez-Huerta, *The Journal of Physical Chemistry C* **2013**, *117*, 20769-20777.

Table 1: Current densities recorded at 0.7 V during the methanol oxidation in the positive going scan for Pt/C, Pt/TiC, Pt/TiCN and Pt/TiN activated up to 0.9 V and 1.0 V

Current density (mA·cm^{-1}) at 0.7 V vs RHE		
	Activated at 0.9 V	**Activated at 1.0 V**
Pt/C	0.11	0.11
Pt/TiC	0.13	0.25
Pt/TiCN	0.15	0.22
Pt/TiN	0.20	0.21

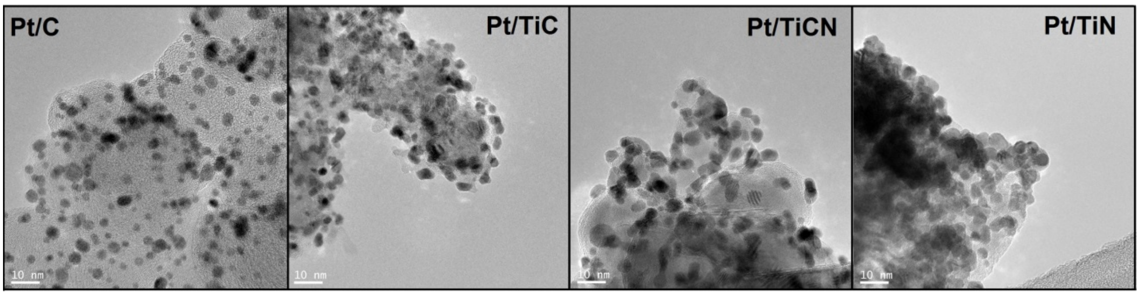

Fig. 1S. TEM images of Pt/C, Pt/TiC, Pt/TiCN and Pt/TiN catalysts

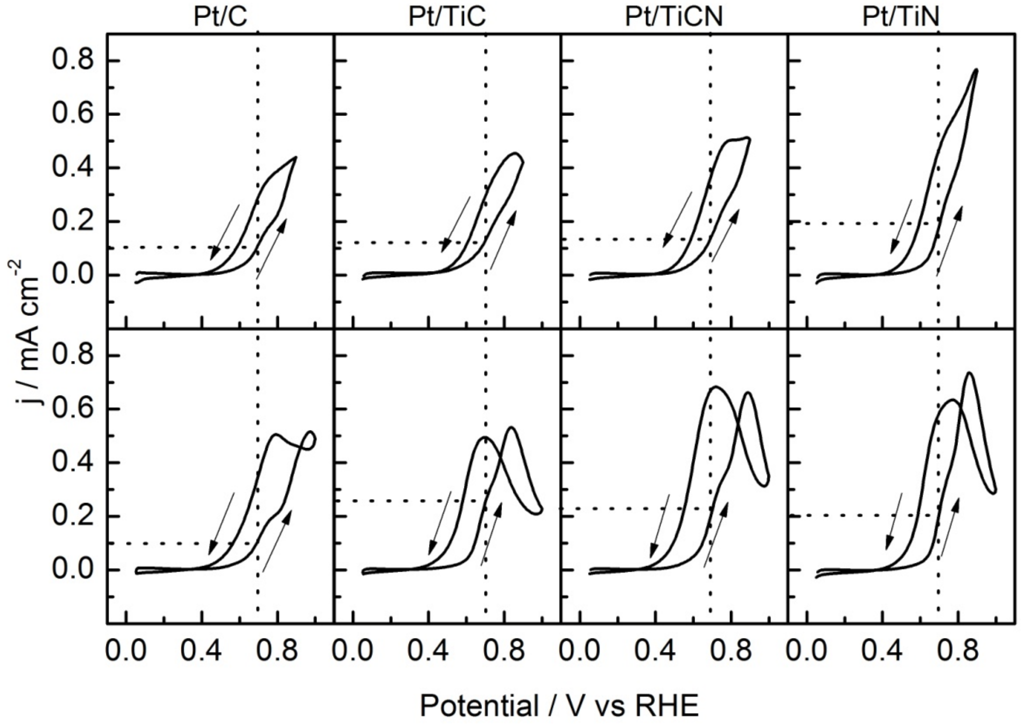

Fig. 2S. Methanol oxidation on Pt/C, Pt/TiC, Pt/TiCN and Pt/TiN recorded in 2 M CH_3OH + 0.5 M H_2SO_4. Scan rate: 20 mv·s^{-1}. Upper panel: catalysts activated up to 0.9 V. Lower panel: catalysts activated up to 1.0 V.

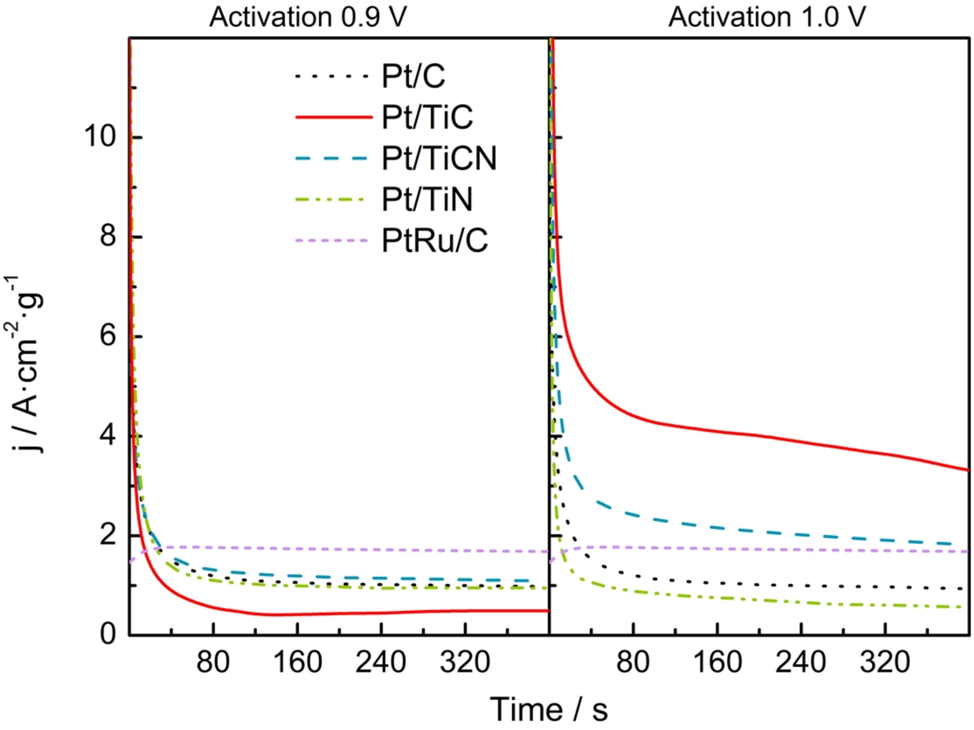

Fig. 3S. Current transients for methanol oxidation on Pt/C, Pt/TiC, Pt/TiCN and Pt/TiN and PtRu/C catalysts in 2 M CH_3OH + 0.5 M H_2SO_4. E_f = 0.55 V. Left panel: catalysts activated up to 0.9 V. Right panel: catalysts activated up to 1.0 V. In order to avoid Ru dissolution, PtRu/C material was only activated up to 0.8 V.