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Coordination complex synthesis of noble metals in the preparation of nanoparticles supported on MWCNTs used as electrocatalysts



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ABSTRACT

Coordination complex salts were synthesized in an aqueous solution and used as precursors to prepare metallic and bimetallic nanoparticles supported on multiwalled carbon nanotubes (MWCNTs) to be applied as electrocatalysts on methanol electrooxidation. The precursors were obtained by the reaction between $(NH_4)_2PtCl_6$, $(NH_4)_2PdCl_6$, $(NH_4)_3RuCl_6$ and HAuCl₄ with tetraoctylammonium bromide (TOAB). These were obtained as $(TOA)_nMCl_y$ salts (where "M" = Pt, Pd, Ru or Au) and were characterized by FT-IR and TGA analysis. The precursors were used to prepare metallic and bimetallic nanoparticles of Pt, Pt–Pd, Pt–Ru, as well as Pt–Au coated on MWCNT (Pt–M/MWCNTs, where M = Pd, Ru or Au). Materials were characterized by TEM, XRD and TGA. The electrocatalytic properties of the Pt–M/MWCNTs electrodes for the methanol oxidation were determined by cyclic voltammetry (CV) and chronoamperometry (CA). The bimetallic nanoparticles presented a higher electrocatalytic activity and stability than the Pt/MWCNTs electrocatalyst, attributed to the addition of "M" which not only led to a smaller average particle size and higher dispersion of Pt of the metallic nanoparticles on MWCNTs but also promoted an elevated electronic transfer between bimetallic nanoparticles.

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1. Introduction

The synthesis of nanostructure materials with controlled size and composition is very important for numerous applications, because of their novel and attractive physical and chemical properties [1], which differ from those properties that exhibited for bulk [2,3]. For example, the transition metal nanoparticles of Pt, Pd, Ru and Au have been studied as catalysts in organic reactions [4-6], as electrocatalysts in fuel cells [7], or as materials with novel electronic [8], chemical sensor [9] and magnetic properties [10]. The catalytic and electronic properties are strongly influenced by the size of the particles, especially in the range 1-10 nm, evidencing the need for size-selective synthesis techniques. The synthesis of metallic and bimetallic nanoparticles is mainly achieved by the chemical reduction of coordination complex salts using different reduction agents such as hydrogen, borohydrides, hydrazine or aldehyde [11–14]. The nanoparticles synthesized by reduction of the coordination complex salts using sodium borohydride as a reducing agent, generally allows the obtaining a very small and uniform particle size because sodium borohydride enables a rapid reduction to afford very small nuclei whose growth and agglomeration is hindered [15].

* Corresponding author. Tel.: +52 646 1744602. E-mail address: jrodrig@cnyn.unam.mx (J.R. Rodriguez). The use of a capping agent improves the control of the size and shape of the nanoparticles, according to the Brust–Schiffrin method [16,17], where the TOAB is used as a capping agent, which permits the preparation of the nanoparticle of 2–3 nm, also this precursor allow to control the morphology of the nanoparticles, which can be spherical or cubic [18–20].

We are interested in the preparation of Pt nanoparticles following the Brust–Schiffrin method, with the aim of controlling their size and surface properties [21–23]. Beside catalysis, the synthesis of coordination complex salts as agent precursors for the preparation of nanoparticles has allowed to acquire nanostructured materials with attractive catalytic properties [24]. In particular, Pt–M nanoparticles have been investigated for their high electrocatalytic activity for methanol oxidation and CO tolerance oxidation related to fuel cell application [25,26].

The present report describes a new promising approach based on the synthesis of new organometallic salts which were characterized by FT-IR and TGA analysis. These salts precursors were used for the preparation of nanoparticles of noble metals to be deposited on MWCNTs and used as electrocatalysts. The materials were characterized by TEM, XRD and TGA. Moreover the Pt–M nanoparticles deposited on MWCNTs (Pt–M/MWCNTs) were studied as electrocatalysts, by cyclic voltammetry (CV) and choronoamperommetry (CA) in the methanol oxidation reaction (MOR).



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2. Experimental

The chemicals used in this study, $(NH_4)_2PtCl_6$ and $(NH_4)_2PdCl_6$, were acquired from Alfa Aesar and HAuCl₄, $(NH_4)_2RuCl_6$, NaBH₄, Tetraoctylammonium bromide (TOAB), and 2-propanol were purchased from Aldrich Co. All chemicals were used without further purification. Triply distilled water was used as dissolvent of the metallic salts.

2.1. Organometallic salts synthesis

The synthesis of the different organometallic salt precursors in this work were obtained by the exchange reaction in an aqueous solution between the ammonium group $[NH_4]^+$ (in the case of $(NH_4)_2PtCl_6$, $(NH_4)_2PdCl_6$ and $(NH_4)_2RuCl_6$) or H⁺ (in the case of HAuCl₄) and $[TOA]^+$, following a similar method reported previously [27]. Eq. (1) shows the general reaction:

$$X_n MCl_v^{n-} + TOAB \to (TOA)_n MCl_v + XBr$$
(1)

(where M = Pt, Pd, Ru, Au, and X = NH_4^+ , H^+)

2.1.1. (TOA)₂PtCl₆ synthesis

Ammonium hexachloroplatinate(IV), $(NH_4)_2PtCl_6$, $(0.3 \text{ g}, 6.76 \times 10^{-4} \text{ mol})$ was dissolved into 20 mL of triply distilled water. This aqueous solution was then added to 25 mL of a TOAB in 2-propanol solution (0.739 g, 1.35×10^{-3} mol) at room temperature. The resulting solution was left under stirring until the complete precipitation of $(TOA)_2PtCl_6$. The product was filtered under vacuum, washed with deionized water, and dried at 70 °C for 8 h. The yield of the $(TOA)_2PtCl_6$ was of 86%.

2.1.2. (TOA)₂PdCl₆ synthesis

Ammonium hexachloropalladate(IV), $(NH_4)_2PdCl_6$, $(0.3 g, 8.45 \times 10^{-4} mol)$ was dissolved into 20 mL of triply distilled water. This aqueous solution was then added to 25 mL of a TOAB in 2-propanol solution (0.924 g, 1.69×10^{-3} mol) at room temperature. The resulting solution was left under stirring until the complete precipitation of $(TOA)_2PdCl_6$. The product was filtered under vacuum, washed with deionized water, and dried at 70 °C for 8 h. The yield of the $(TOA)_2PdCl_6$ was of 91%.

2.1.3. (TOA)AuCl₄ synthesis

Gold(III) chloride hydrate, HAuCl₄·3HO, (0.3 g, 7.62×10^{-4} mol) was dissolved into 20 mL of triply distilled water. This aqueous solution was then added to 25 mL of a TOAB in 2-propanol solution (0.417 g, 7.62×10^{-4} mol) at room temperature. The resulting solution was stirred until the formation of a (TOA)AuCl₄ precipitate. The product was filtered under vacuum, washed with deionized water, and dried at 70 °C for 8 h. The yield of the (TOA)AuCl₄ was of 77%.

2.1.4. (TOA)₂RuCl₆ synthesis

Ammonium hexachloruthenate(IV), $(NH_4)_2RuCl_6$, $(0.3 g, 8.57 \times 10^{-4} \text{ mol})$ was dissolved into 20 mL of triply distilled water. This aqueous solution was then added to 25 mL of a TOAB in 2-propanol solution (0.937 g, 1.71×10^{-3} mol) at room temperature. The resulting solution was left under stirring until the complete precipitation of $(TOA)_2RuCl_6$. The product was filtered under vacuum, washed with deionized water, and dried at 70 °C for 8 h. The yield of the $(TOA)_2RuCl_6$ was of 78%.

2.2. MWCNTs synthesis

The MWCNTs used in this work were obtained by spray pyrolysis following a similar method reported elsewhere [28]. The starting solution was composed of ferrocene (1.0 g, Alfa Aesar 98.0%) as catalyst which is dissolved in 25 mL of toluene (Fulka 99.5%). This solution was atomized and carried by a flow of argon into a Vycor tube that is heated in a cylindrical furnace equipped with a high precision temperature controller (\pm 1 °C). The furnace temperature was set at 900 °C and the flow rate was regulated at 75 mL/s. The solution was fed for 30 min. A black film of MWCNTs was then formed at the inner surface of the Vycor tube and was mechanically removed and collected. The crude MWCNTs (0.5 g) were added to 20 mL of a HNO₃ solution (Aldrich, 70%). The mixture was placed in an ultrasonic bath for 1 h and then stirred for 12 h while it refluxed. The product was filtered under vacuum, washed with deionized water, and dried at 70 °C for 8 h.

2.3. NPs/MWCNTs

The nanoparticles of Pt, Pt–Pd, Pt–Au and Pt–Ru (with atomic ratio Pt:M, 1:1) *in situ* synthesized on the MWCNTs surface from the metallic precursors $(TOA)_nMCl_y$, is described as follows. In the first step, MWCNTs (25 mg) were added to 25 mL of 2-propanol and dispersed in an ultrasonic bath for 1 h. In a second step, 3.13×10^{-5} mol of the metal precursor in 5 mL of 2-propanol solution was added to the MWCNTs suspension and stirred for 1 h. Finally, in the third step, 10 mL of an aqueous solution of NaBH₄ in excess (stoichiometric metal:NaBH₄ ratio = 1:10) was added by drip during 5 min to the suspension of $(TOA)_nMCl_y/MWCNTs$, which was stirred at room temperature for 12 h. The mixture obtained was then filtered, washed with acetone and water, and finally dried at 70 °C for 4 h. In this step the reaction reduction occurred to obtain NPs/MWCNTs as shown in Eq. (2).

$$(TOA)_nMCl_y + NaBH_4 + MWCNTs$$

 $\rightarrow M/MWCNTs + (Solution : (TOA)^+Cl, NaCl, B(OH)_3)$ (2)

(Where M = Pt, Pd, Ru, Au)

2.4. Electrode preparation

The catalysts' electrodes were prepared with 2 mg of Pt/ MWCNTs or bimetallic Pt–M/MWCNTs, 150 µL of Nafion (Aldrich, 5%) and 550 µL of ethanol (Aldrich, 99.5%) and mixed ultrasonically. A measured volume (5 µL) of this ink was deposited using a micro-pipette onto a glassy carbon (GC) electrode (BAS, 3 mm in diameter) which was first polished with alumina powder, followed by 2 min sonication in water. The catalyst ink was then dried at 40 °C in an oven. Each electrode contained about 4.97×10^{-4} mmol of the metal catalyst.

2.5. Characterization

Organometallic salts were characterized by infrared spectroscopy (FT-IR) using a Perkin-Elmer FTIR 1605 spectrometer and the thermogravimetric analysis (TGA) was performed using a TA-Instruments SDT 2920. Samples were heated in a platinum-pan under dry air flux from room temperature up to 700 °C (heating rate: 5 °C/min). The NPs/MWCNTs, X-ray diffraction (XRD) studies were performed using a Phillips XPert Diffractometer, with a Cu Kα (λ = 1.5405 Å) radiation source operated at 45 kV and 40 mA. All samples were evaluated in a range from 10 at 70 of 2 θ , and the crystalline phases were identified using a database JCPDS-ICDD 2003. The morphology of metallic NPs supported on MWCNTs was studied by transmission electron microscopy (TEM) using a JEOL 2010 microscope. Samples were dispersed ultrasonically in ethanol and a drop of suspension was placed onto a holey carbon-coated Cu grid and it was allowed to dry. The images were



Fig. 1. FT-IR spectrum of the (TOA)₂RuCl₆ compound.

obtained in a transmission electron microscopy (TEM) mode using a bright field (BF). The Pt–M/MWCNTs, TGA studies were performed in a dry air flux atmosphere to oxidize them. In this case, MWCNTs supported samples were heated at 5 °C/min from room temperature to 700 °C. The electrochemical measurement were performed using an EC Epsilon BAS potentiostat/galvanostat and a conventional three electrode electrochemical cell, using a glassy carbon electrode as a working electrode (BAS, 3 mm diameter), a Pt electrode as a counter electrode and a Ag/AgCl electrode as a reference electrode. All the solutions were prepared using H₂SO₄ (Fermont, 98%), methanol (Aldrich, 99.5%) and ultrapure water (Millipore MilliQ, 18 M Ω cm).

3. Results and discussion

3.1. Characterization of the organometallic salts

3.1.1. FT-IR study

Fig. 1 shows the infrared spectrum corresponding to the (TOA)₂₋ RuCl₆ structure, whereas Table 1 summarizes the infrared frequencies detected on the different organometallic precursors with their corresponding modes of vibration. The IR spectrum of (TOA)₂RuCl₆ presents four main groups of vibration corresponding to the TOA group at 724, 1468, 2853, and 2924 cm⁻¹. Close frequency values were generally acquired on the other organometallic precursors (Table 1) confirming a relative similar arrangement in all cases. The bands at 2924 and 2853 cm⁻¹ are assigned to the asymmetric and symmetric C-H respectively, due to stretching vibrations of the methylene (CH₂) group of the TOA. A small shoulder around 2924 cm⁻¹ is due to the asymmetric C–H stretch of the methyl (CH_3) group. The band observed at 1468 cm⁻¹ is attributed to the asymmetric C-H scissoring vibration of the CH₂-N⁺ whereas the band at 724 cm⁻¹ corresponds to a rocking mode vibration of the CH₂ chain. If these bands are compared to those obtained from the TOAB molecule [29], the C-H stretching vibration bands of the methylene chain are similar to those shown in Table 1. At the same time very similar band positions were found for (TOA)₂₋ PtCl₆, (TOA)₂PdCl₆ and (TOA)AuCl₄. These unchanged frequencies show that the conformation of the methylene chain is maintained in the as-formed organic salt.

3.1.2. TGA study

TGA was performed to confirm the stoichiometry of the as-prepared different organometallic salts and to investigate their respective thermal decomposition mechanisms. For this purpose it was assumed that organometallic salts presented a similar degree of decomposition, as the decomposition took place in an

FT-IR frequencies observed for the different organometallic salts.

Compound	IR frequenc	IR frequencies (cm ⁻¹)			
	$v_{\rm as}$ (CH ₂)	<i>v</i> _s (CH ₂)	δ (C–H) of N–(CH ₂) ₄	β-(CH ₂)	
(TOA) ₂ PtCl ₆ (TOA) ₂ PdCl ₆ (TOA)AuCl ₄ (TOA) ₂ RuCl ₆ TOAB[29]	2924 2921 2920 2924 2925	2853 2852 2854 2853 2859	1481 1471 1476 1468 1458	725 723 721 724 714	

oxygen atmosphere; the final residue is assumed to be in the oxide form. The detailed analysis of the thermal decomposition mechanisms and the resulting stoichiometry for each organometallic salt is discussed below.

The thermal decomposition profile of the ruthenium salt is shown in Fig. 2. Up to two different decomposition steps can be recognized in the first-derivative curve of the weight loss at average temperatures of 180–280 °C and 280–375 °C. Table 2 summarizes the different weight losses observed for each step and the possible molecules eliminated during the treatment under oxygen. In the first step, the experimental weight loss observed corresponds to the removal of $8(CH_3(CH_2)_5CH=CH_2)$, $2NH_4Cl$ and Cl_2 that result from the disproportionation of the radicals. The second step corresponds to the elimination of Cl_2 with a final Ru_2O_3 residue suggesting that a reduction process occurs around 280-375 °C. There is a cumulative weight loss of 90.3% and the residual weight corresponds to a Ru_2O_3 formula.

The thermal decomposition of the platinum salt shows two steps of weight loss that can be distinguished at average temperatures of 240–350 °C and 350–480 °C (Supplementary material Fig. S1). A detailed analysis of weight loss percentages and possible molecules that were eliminated in each step are shown in Table S1 (supplementary material). The first step corresponds to the loss of the main parts of the hydrocarbons $8(CH_3(CH_2)_5CH=CH_2)$ that results from the disproportionation of radicals with a weight loss of 66%. The second step is related to the removal of the remnant of the two ammonium groups ($2NH_4CI$) and of the two chloride molecules ($2Cl_2$) leading to a theoretical weight loss of 18%. The chemical formula of the residue is PtO_2 suggesting that Pt is still present at an oxidation state of IV.

The thermal decomposition profile of the palladium salt is shown in Fig. S2 (supplementary material). Up to two different decomposition steps can be recognized in the first-derivative curve of the weight loss at average temperatures of 170–330 °C and 330–470 °C. Table S2 (supplementary information), summarizes



Fig. 2. TGA analysis under a dry air flux atmosphere of the $(TOA)_2RuCl_6$ compound. Sample was heated at 5 °C/min from room temperature to 700 °C. Weight loss and its first derivative curves.

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Table 2

TGA results for the $(\mathrm{TOA})_2\mathrm{RuCl}_6$ compound decomposition under a dry air flux atmosphere.

	(TOA) ₂ RuCl ₆
<i>T</i> ₁ (°C)	180-280
Δw_1 , wt.% (exp)	83.5
Δw_1 , wt.% (theor)	83.4
Assuming loss	$8(CH_3(CH_2)_5CH=CH_2) + 2NH_4Cl + Cl_2$
T ₂ (°C)	280-375
Δw_2 , wt.% (exp)	6.8
Δw_2 , wt.% (theor)	6.9
Assuming loss	Cl ₂
$\sum \Delta w$, wt.% (exp)	90.3
Residual, wt.% (exp)	9.7
Residual, wt.% (theor)	9.7
Assuming residual as Ru ₂ O ₃	

the different weight losses observed for each step and the possible molecules eliminated during the treatment under oxygen. In the first step, the experimental weight loss observed corresponds to the removal of $6(CH_3(CH_2)_4CH=CH_2)$ and $2(CH_3(CH_2)_5CH=CH_2)$ that results from the disproportionation of the radicals. As for the preceding cases, the second step corresponds to the elimination of the $2(CH_3CH_2)_3N$ and $3Cl_2$ with a final PdO₂ residue suggesting that a reduction process occurs around 330-470 °C. A cumulative weight loss of 87.3% corresponds to the elimination of all the organic part of the organometallic salt to obtain PdO₂ suggesting that Pd is still present at the oxidation state of IV. The discrepancies between the theoretical and experimental weight losses were -1.0% and -1.3% for the precursor salts of Pt and Pd, respectively.

The TGA curve and its first-derivate signal for the gold salt are presented in Fig. S3 (supplementary material). Two decomposition steps can be noticed at 200–335 °C and 335–490 °C. The analysis of the weight loss and the possible products eliminated are summarized in Table S3 (supplementary material section). The first step corresponds to the removal of the main parts of the hydrocarbons $3(CH_3(CH_2)_4CH=CH_2)$ and $(CH_3(CH_2)_5CH=CH_2)$ that result from the disproportionation of radicals, corresponding a weight loss of 49%. In the second step, the weight loss is the ratio between the amount removed to the remnant of $(CH_3)_3N$ and $2Cl_2$ being 24.2%. The chemical formula of the residue is Au_2O_3 suggesting that Au is still present at an oxidation state of III.

3.2. Nanoparticles on MWCNTs

3.2.1. XRD study,

To obtain the crystallographic information of the electrocatalysts, the powder X-ray diffraction technique was used. The XRD patterns (Fig. 3) for Pt–M/MWCNTs catalysts show three diffraction peaks at the Bragg angles of 39.8, 45.7 and 67.7 corresponding to the (111), (200) and (220) planes of Pt face-centered cubic (fcc) crystal structure. The diffraction peaks in the samples are slightly shifted to higher 2θ values with respect to the corresponding peaks reported in the database JCPDS file No. 04-0802. This was due to the fact that the diffraction patterns were obtained with the powder mode and the samples were characterized in form of stacked sheets. The diffraction peak at 26.4 corresponds to the (002) plane of C support, reported in the database JCPDS file No. 08-0415. Table 3 lists the calculated average sizes of nanoparticles supported on MWCNTs which were calculated from the FWHM of (111) peak using the Scherrer equation [30,31].

3.2.2. TEM study

Micrographs of the Pt–M/MWCNTs were obtained from the TEM mode using a BF image detector. Fig. 4 shows low magnification

TEM images of the MWCNTs supported nanoparticles obtained from Pt, Pt-Pd, Pt-Au, and Pt-Ru catalysts. It can be seen that for all samples, the Pt-M nanoparticles were uniformly formed on the external wall of the MWCNTs; these nanoparticles showed spherical morphologies in all materials. Well-dispersed Pt-M nanoparticles can be found in any microregion of the sample viewed from the TEM grid. Their sizes were obtained by measuring the nanoparticles from the TEM images using an imaging analysis software digital micrograph (Gatan, Inc.). More than 300 nanoparticles were measured to ensure statistically significant representation of the nanoparticles sizes (Table 3). The Pt-M had a mean size of less than 2 nm, except for Pt-Ru which had a mean size of less than 3 nm. The size distributions of these Pt-M nanoparticles (Fig. 4) are fairly consistent with a Gaussian distribution, obtaining a geometric mean of 1.7, 1.4, 1.8 and 2.3 for the samples Pt. Pt-Pd. Pt-Au and Pt-Ru, respectively, showing that the nanoparticles of the Pt-Ru had the largest particles and broadest size distribution. Thus, these values of the mean particle size are different to those obtained by XRD analysis, but the behavior of the particle size is the same, because the TEM study relies on a statistical analysis from values of mean particle size deposited on MWCNTs and the particle size obtained by XRD characterization is calculated with Scherrer equation which is not as accurate for nanoparticles.

3.2.3. TGA study

TGA were performed under a dry air flux, for the different Pt–M/ MWCNTs metallic systems to quantify the amount of metal deposited on the support. Fig. 5 reports the different TGA curves for the Pt–M/MWCNTs systems, whereas quantification results are listed in Table 4. The onset and final temperatures for the oxidation process are also reported in Table 4. For Pt/MWCNTs (solid line), the beginning of the oxidation of the support is observed at 426 °C. The oxidation is completed at 655 °C. Only a residual mass (14 wt.%) of the initially loaded Pt/MWCNTs sample is found at the end of the oxidative treatment. This residue corresponds to PtO₂ coming from the (TOA)₂PtCl₆. For Pt–Pd/MWCNTs (dash line), the beginning of the oxidation of the support is observed at 435 °C and the oxidation is completed at 645 °C. Only a residual mass (19 wt.%) of the initially loaded Pt–Pd/MWCNTs sample is found



Fig. 3. Powder XRD patterns of the electrocatalysts supported on MWCNTs: Pt, Pt–Pd, Pt–Au and Pt–Ru, recorded from 10 at 70 of 20.

Table 3

Average particle size of catalysts from XRD and TEM data of Figs. 3 and 4, respectively.

Compound	Average particle size XRD (nm)	Surface area (cm ² /g) [31]	Average particle size TEM (nm)	Standard deviation, σ (nm)
Pt/MWCNTs	3.7	76	1.7	0.4
Pt-Pd/MWCNTs	2.5	112	1.4	0.2
Pt-Au/MWCNTs	4.4	64	1.8	0.2
Pt-Ru/MWCNTs	4.2	67	2.3	0.5



Fig. 4. Transmission electron micrographs of (a) Pt/MWCNTs, (b) Pt-Pd/MWCNTs, (c) Pt-Au/MWCNTs, (d) Pt-Ru/MWCNTs.

at the end of the oxidative treatment. This residue corresponds to PtO_2 and PdO_2 coming from the precursor salts. For Pt-Au/MWCNTs (dot line) and Pt-Ru/MWCNTs (dash-dot line), the beginning of the oxidation of the support is observed at 402 °C for both samples. The oxidation is completed at 633 °C for the sample that contains Au and 634 °C for the one that contains Ru. The residual mass (11 wt.%) of the initially loaded Pt-Au/MWCNTs sample is found at the end of the oxidative treatment; a similar procedure was followed by Pt-Ru/MWCNTs obtaining a residual mass of 17 wt.%. For sample Pt-Au/MWCNTs the residue corresponds to PtO_2 and Ru_2O_3 and for Pt-Ru/MWCNTs the residues correspond to PtO_2 and Ru_2O_3 . In both cases, the samples residues correspond to metal oxides coming from the precursor salts.

For Pt–Au/MWCNTs and Pt–Ru/ MWCNTs, the onset of the oxidation process starts at lower temperatures than for the Pt/ MWCNTs and Pt–Pd/MWCNTs catalysts. Contrary to Pt and Pt–Pd containing solids, Pt–Au and Pt–Ru effectively catalyzes the oxidation of the MWCNTs. This effect is due to the oxygen species formed on Pt–Au and Pt–Ru which are transferred to the carbon surface thanks to an intimate contact between Pt–M and C



Fig. 5. TGA analyses under a dry air flux atmosphere of the different Pt–M/ MWCNTs systems. Sample was heated at $5 \,^{\circ}$ C/min from room temperature to 700 °C. Weight loss curves.

Table 4 TGA results for the Pt-M/MWCNTs systems decomposition under a dry air flux atmosphere.

Compound	Onset T _{oxid} (°C)	Final T _{oxid} (°C)	Residual metal oxide amount (wt.% exp)	Residual metal oxide amount (wt.% theor)
Pt/MWCNTs	426	655	14 (PtO ₂)	22 (PtO ₂)
Pt-Pd/MWCNTs	435	645	19 (PtO ₂ , PdO ₂)	19 (PtO ₂ , PdO ₂)
Pt-Au/MWCNTs	402	633	11 (PtO ₂ , Au ₂ O ₃)	22 (PtO ₂ , Au ₂ O ₃)
Pt-Ru/MWCNTs	402	634	17 (PtO ₂ , Ru ₂ O ₃)	19 (PtO ₂ , Ru ₂ O ₃)

resulting in the formation of CO₂. Pt-M is definitely oxidized into $PtO-MO_x$ only after the complete oxidation of the carbon support [32]. The final oxide residue corresponds to a 10 wt.% of Pt theoretical loading on bimetallic systems and of 20 wt.% of Pt theoretical loading on a metallic system. This leads to a relatively low yield of deposited Pt-M (Table 4) during the preparation of the Pt-M/ MWCNTs solid. Therefore, the very high achieved dispersion of Pt-M nanoparticles with an average size of 1.7 nm observed by TEM is compensated by the difficulties to deposit selectively Pt-M on MWCNTs using the $(TOA)_n M_x Cl_v^{n-}$ salts.

It should be underlined that metal deposition on the MWCNTs support is more or less directly related to the stability of the different organometallic salts used and particularly to the strength of the interaction between the polar headgroup of the TOA moiety and the metal chloride anions. A stronger interaction between the hydrophobic TOA group and the metallic anions seems to decrease the anchoring of the organometallic salt on the MWCNTs support after reduction by NaBH₄ and before loading of the NP's. This is the case for Pd and Ru showing a low stability of their respective precursors compared to Pt and Au (Table 4). The selective deposition of the different metals on the MWCNTs support will therefore partly depend on the respective stabilities of the organometallic salts [23].

3.3. Electrochemical evaluation

30

20

10

0

Before the evaluation of the electrochemical activity of Pt-M/ MWCNTs catalysts, 30 scans were performed to clean the surface of the Pt-M/MWCNTs electrodes within a potential range from -0.2 to 1.3 V at a scan rate of 100 mV s⁻¹ in a 0.5 M H_2SO_4 solution saturated with N₂ [33,34]. The CV curves looked similar to those of pure Pt polycrystalline (Fig. 6). However, the hydrogen adsorption/ desorption region presented a shift to higher potentials for bimetallic Pt-M catalysts. This was caused by a change of the lattice parameters of the crystal structure of Pt, due to the incorporation of the second metal, which promoted changes in the adsorption strength of the hydrogen species on the Pt because the Pt-M

Pt/MWCNTs

Pt-Pd/MWCNTs

Pt-Au/MWCNTs

Pt-Ru/MWCNTs

material is more electropositive that Pt polycrystalline, thus modifying the electronic environment and therefore the adsorption strength of protons. Moreover Fig. 6 shows that Pt, Pt-Ru and Pt-Au do not exhibit an oxidation peak between 0.4 and 0.45 V in contrast to Pt-Pd, which is possibly due to the OH-adsorbed species on Pd present on the surface of the nanoparticles. At the same time in the cathodic scan it can be observed a shift in the peak of the OH-desorbed species of the Pt-Pd surface at 0.1 V (0.3 V) compared to Pt, Pt-Ru and Pt-Au which appeared at 0.37, 0.37 and 0.4 V. This is because the Pt-Pd material is more electropositive and the OH-adsorbed species is stronger for Pd [35].

3.3.1. Methanol oxidation

To evaluate the activity of Pt/MWCNTs and Pt-M/MWCNTs catalvsts toward the methanol electrooxidation. cvclic voltammogram experiments were performed in a 1 M MeOH solution in 0.5 M H₂SO₄ (potential range between 0.2 and 1.3 V) [36,37]. The cycling was repeated until a reproducible CV curve was obtained before the measurement curves were recorded. As seen in Fig. 7, in the forward scan, methanol oxidation produced a prominent symmetric anodic peak for Pt/MWCNTs at 1.239 V (versus Ag/AgCl) with 56.2 mA mg⁻¹Pt (Table 5). The incorporation of the second metal in the Pt-M/MWCNTs systems induced a catalytic effect on the methanol electrooxidation: Pt-Pd/MWCNTs catalyst oxidized methanol at 0.960 V, Pt-Au/MWCNTs at 0.807 V and Pt-Ru/ MWCNTs at 0.809 V. In the reverse scan, an anodic peak was detected with a current density (j_b) , attributing this anodic peak in the reverse scan to the removal of the incompletely oxidized carbonaceous species formed on the forward scan [38]. Hence the ratio of the forward anodic peak with current density $j_{\rm f}$ to the reverse anodic peak with current density $j_{\rm b}$, $(j_{\rm f}/j_{\rm b})$ can be used to describe the catalyst tolerance to carbonaceous species accumulation. A low j_f/j_b ratio indicates poor oxidation of methanol to carbon dioxide during the anodic scan and an excessive accumulation of carbonaceous residues on the catalyst surface. On the other hand, a high j_f/j_b ratio shows the inverse case. Pt-Pd/MWCNTs and Pt-Au/ MWCNTs catalysts were the systems with higher j_f/j_b ratios.



Fig. 6. Cyclic voltammograms of Pt-M/MWCNTs catalysts in 0.5 M H₂SO₄ solution saturated by N₂ at 25 °C, recorded at 100 mV s⁻¹



Fig. 7. Cyclic voltammograms of Pt-M/MWCNTs catalysts performed with 1 M methanol in 0.5 M sulfuric acid at 25 °C. Scan rate: 100 mV s

 Table 5

 Oxidation peaks of cyclic voltammograms of the Pt-M/MWCNTs systems.

Compound	$E_{\rm f}$	$j_{ m f}$	E _b	$j_{ m b}$	$j_{ m f}/j_{ m b}$
Pt/MWCNTs	1239	56.2	676	38.8	1.45
Pt-Pd/MWCNTs	960	53.7	508	30.9	1.74
Pt-Au/MWCNTs	807	30.0	370	16.6	1.81
Pt-Ru/MWCNTs	809	27.4	437	21.6	1.27

The catalytic stability of the Pt/MWCNTs and Pt–M/MWCNTs were examined using chronoamperometry. Fig. 8a) shows the chronoamperometric curves of 1 M MeOH in a 0.5 M H₂SO₄ solution for Pt/MWCNTs and Pt–M/MWCNTs catalyst electrodes at a fixed potential of $E_{\rm f}$. For all catalysts the potentiostatic current decreases rapidly at the initial stage, which might be due to the formation of intermediate species, such as CO_{ads} and CHO_{ads} etc., during the methanol oxidation reaction [39]. Gradually, the current decayed and a pseudo-steady state was achieved. The current density of Pt–Pd/MWCNTs was higher than that of Pt–Ru/MWCNTs and this in turn greater than that of Pt/MWCNTs and of Pt–Au/MWCNTs catalyst electrodes during the whole testing time indicating that the electrocatalytic stability of Pt–Pd/MWCNTs catalyst for the methanol oxidation was also higher than that of the other catalysts probed.

The linear decay of the current at times greater than 500 s may be characterized by the long time poisoning rate [40], δ :

$$\delta = (100/i_0)(di/dt)_{t>500 \text{ s}} / \% \text{s}^{-1}$$
(3)

where $(di/dt)_{t > 500 \text{ s}}$ is the slope of the linear portion of the current decay, and i_o is the current at the start of the polarization. In Fig. 8b) the variation of this parameter (δ) is plotted as a function of the



Fig. 8. (a) Chronoamperommetry and (b) poisoning rate of the Pt–M/MWCNTs catalysts for the oxidation of 1 M methanol in a 0.5 M sulfuric acid solution saturated with N_2 at 25 °C.

catalyst type (Pt–M/MWCNTs). An effect is seen upon adding a second metal to the Pt surface, with a decrease in the poisoning rate from $\delta = 0.030\% \text{ s}^{-1}$ for Pt/MWCNTs catalyst to $\delta = 0.028\% \text{ s}^{-1}$ for Pt–Au/MWCNTs. Pt–Pd/MWCNTs and Pt–Ru/MWCNTs catalysts were poisoned much less than the catalyst Pt–Au/MWCNTs, with a poisoning rate of 0.017 and 0.016% s⁻¹, respectively.

4. Conclusions

New organometallic salts: (TOA)₂PtCl₆, (TOA)₂PdCl₆, (TOA)₂-RuCl₆, (TOA)AuCl₄ were successfully synthesized and characterized by FT-IR and TGA studies. As shown by TEM characterization, these precursors were used in a second step to prepare Pt-M/MWCNTs electrocatalysts presenting very high dispersion and small average particle sizes (particularly Pt-Pd) with similar metal loading. Pt-based binary electrocatalysts consisting of Pd, Au and Ru were prepared by the co-precipitation method at room temperature. The binary electrocatalysts showed higher activities and enhanced CO relative tolerance than Pt/MWCNTs. The best performance was developed by the binary Pt-Pd/MWCNTs electrocatalyst. The second metal (in this case Pd) promoted an increase in the adsorption of OH⁻ species because Pd is more hydrophilic that platinum; coupled with this, Pd had an electronegativity different from that of Pt, which also modified the bond strength between Pt and CO species due to electronic effects.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2013.06.042.

References

- [1] G. Schmid, Chem. Rev. 92 (1992) 1709.
- [2] M.A. El-Sayed, Acc. Chem. Res. 34 (2001) 257.
- [3] G. Schmid, M. Bäumle, M. Geerkens, I. Heim, C. Osemann, T. Sawitowski, Chem. Soc. Rev. 28 (1999) 179.
- [4] H. Bönnemann, G. Braun, W. Brijoux, R. Brinkmann, A.S. Tilling, K. Seevogel, K. Siepen, J. Organomet. Chem. 520 (1996) 143.
- [5] J.D. Aiken, R.G. Finke, J. Mol. Catal. A: Chem. 145 (1999) 1.
- [6] H. Bönnemann, R.M. Richards, Eur. J. Inorg. Chem. 10 (2001) 2455.
- [7] X. Ren, P. Zelenay, S. Thomas, J. Davey, S. Gottesfeld, J. Power Sources 86 (2000) 111.
- [8] T. Oku, K. Suganuma, Chem. Commun. 23 (1999) 2355.
- [9] Y. Imai, Y. Kimura, M. Niwano, Appl. Phys. Lett. 101 (2012) 181907.
- [10] M. Chen, J. Kim, J.P. Liu, H. Fan, S. Sun, J. Am. Chem. Soc. 128 (2006) 7132.
- [11] T.S. Ahmadi, Z.L. Wang, T.C. Green, A. Henglein, M.A. El-Sayed, Science 272 (1996) 1924.
- [12] K. Wikander, C. Petit, K. Holmberg, M.P. Pileni, Langmuir 22 (2006) 4863.
- [13] K. Esumi, M. Shiratori, H. Ishizuka, T. Tano, K. Torigoe, K. Meguro, Langmuir 7 (1991) 457.
- [14] C. Wang, J. Yang, Y. Ding, Prog. Nat. Sci. (2013). in press.
- [15] M.J. Hossain, H. Tsunoyama, M. Yamauchi, N. Ichikuni, T. Tsukuda, Catal. Today 183 (2012) 101.
- [16] M. Brust, M. Walker, D. Bethell, D.J. Schiffrin, R. Whyman, J. Chem. Soc., Chem. Commun. 7 (1994) 801.
- [17] J. Yang, E.H. Sargent, S.O. Kelley, J.Y. Ying, Nat. Mater. 8 (2009) 683.
- [18] A. Demortiére, P. Launois, N. Goubet, P. Albouy, C. Petit, J. Phys. Chem. B 112 (2008) 14583.
- [19] A. Demortiére, C. Petit, Langmuir 23 (2007) 8575.
- [20] H. Chan, A. Demortiére, L. Vukovic, P. Král, C. Petit, J. Am. Chem. Soc. Nano 6 (2012) 4203.
- [21] G. Alonso, L. Morales, E. Rogel, E. Reinoso, A. Licea, R.M. Felix, G. Berhault, F. Paraguay, J. Nanopart. Res. 13 (2011) 3643.
- [22] R. Richards, R. Miirtel, H. Biinnemann, Fuel Cells Bull. 37 (2001) 7.
- [23] M.T. Reetz, W. Helbig, J. Am. Chem. Soc. 116 (1994) 7401.

- [24] Y. Gochi, G. Alonso, N. Alonso, Electrochem. Commun. 8 (2006) 1487.
- [25] I.R. Moraes, W.J. Silva, S. Tronto, J.M. Rosolen, J. Power Sources 160 (2006) 997. [26] A. Habrioux, D. Diabaté, J. Rousseau, T.W. Napporn, K. Servat, L. Guétaz, A. Trokourey, K.B. Kokoh, Electrocatalysis 1 (2010) 51.
- [27] J. Yang, J.Y. Lee, J.Y. Ying, Chem. Soc. Rev. 40 (2011) 1672.
- [28] A. Aguilar, W. Antúnez, G. Alonso, F. Paraguay, F. Espinosa, M. Miki, Diam. Relat. Mater. 15 (2006) 1329.
- [29] S.S. Nair, S.A. John, T. Sagara, Electrochim. Acta 54 (2009) 6837.
- [30] A. Khorsand, W.H. Majid, M.E. Abrishami, R. Parvizi, Solid State Sci. 14 (2012) 488.
- [31] A. Pozio, M. Francesco, A. Cemmi, F. Cardellini, L. Giorgi, J. Power Sources 105 (2002) 13.
- [32] R. Sellin, J.M. Clacens, C. Coutanceau, Carbon 48 (2010) 2244.

- [33] W.S. Li, L.P. Tian, Q.M. Huang, H. Li, H.Y. Chen, X.P. Lian, J. Power Sources 104 (2002) 281.
- [34] B. Habibi, N. Delnavaz, Int. J. Hydrogen Energy 36 (2011) 9581.
- [35] T. Lei, M.S. Zei, G. Ertl, Surf. Sci. 581 (2005) 142.
- [36] M.K. Motlagh, M. Noroozifar, M.S. Kakhki, Int. J. Hydrogen Energy 36 (2011) 11554.
- [37] W. Ye, H. Kou, Q. Liu, J. Yan, F. Zhou, C. Wang, Int. J. Hydrogen Energy 37 (2012) 4088.
- [38] R. Manoharan, J.B. Goodenough, J. Mater. Chem. 2 (1992) 875.
 [39] A. Kabbabi, R. Faure, R. Durand, B. Beden, F. Hahn, J.M. Leger, C. Lamy, J. Electroanal. Chem. 444 (1998) 41.
- [40] C.L. Green, A. Kucernak, J. Phys. Chem. B 106 (2002) 11446.