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# Journal of Alloys and Compounds



journal homepage: www.elsevier.com/locate/jallcom

# Pt nanoparticles on titania nanotubes prepared by vapor-phase impregnation-decomposition method

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#### ARTICLE INFO

Article history: Received 9 July 2008 Received in revised form 27 October 2009 Accepted 27 October 2009 Available online 4 November 2009

*Keywords:* Titania Nanotubes Platinum nanoparticles

1. Introduction

# ABSTRACT

Platinum (Pt) nanoparticles were prepared on titania nanotubes (TNTs) by vapor-phase impregnation-decomposition method using platinum acetylacetonate as precursor. TNTs and Pt precursor were mixed in 3:1 weight ratio before vapor-phase impregnation. The mixed powders were heated at 453 K for 10 min to evaporate the precursor in a horizontal tube quartz reactor at a total pressure of 66.6 kPa. Then, the impregnated TNTs were moved to a higher temperature zone (673 K) inside the tube reactor to achieve the precursor decomposition. HAADF-STEM observations, AAS and XPS results revealed that this method allows the formation of uniformly distributed Pt nanoparticles on the surface of TNTs with a narrow distribution of particle size (2.1 nm mean size). Pt nanoparticles remain mainly as  $Pt^0$  oxidation state with a  $Pt^0/Pt^{2+}$  atomic ratio of 3.9.

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The interest in titania nanotubes (TNTs) has grown explosively in the last decade because of their high technological potential in diverse areas such as in solar energy conversion [1], hydrogen sensing [2], lithium storage [3], photocatalysis [4], biocompatibility [5,6] and catalysis [7,8]. Titania nanotubes or nanofibers obtained by a hydrothermal treatment in NaOH solution exhibit specific surface areas as large as  $400 \text{ m}^2/\text{g}$  as a result of their internal and external porosities. As a consequence, over the past 5 years, these types of titania nanotubes have been investigated as large surface area supports of a variety of catalytic species including noble metals and metallic oxides [3,7,9]. For example, Pt nanoparticles have been incorporated on titania nanotubes to improve the selective oxidation of different compounds [9-12] and hydrogenation processes [13,14]. Well-dispersed nanoparticles ranging from 1 to 20 nm depending on their chemical nature and the deposition conditions have been obtained on titania nanotubes. Conventional wet impregnation has been the most frequently employed method to incorporate the catalytic species on the titania nanotubes. However, other methods such as metal organic chemical vapor deposition (MOCVD) or alternatively the vaporphase impregnation-decomposition method can be considered to deposit the catalytic species on the titania nanotubes. Both methods

doi:10.1016/j.jallcom.2009.10.232

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have proved to be successful in obtaining metallic nanoparticles on powdered supports [15–18]. The former method allows the deposition of the catalytic nanoparticles in only one-single step, but a fluidized bed reactor is required. In contrast, the latter method which includes two-step process that consist of (i) the vapor-phase impregnation of the precursor on the support followed by (ii) the thermal activation to decompose the precursor, does not require a fluidized bed reactor. To the best of our knowledge, we have used for the first time the vapor-phase impregnation–decomposition method to incorporate Pt nanoparticles on TNTs leading to much better characteristics than those obtained by conventional wet impregnation.

#### 2. Experimental

TNTs were prepared by the hydrothermal treatment in a NaOH solution previously reported [19]. TiO<sub>2</sub> powder in anatase phase was used as the raw material for the nanotube preparation. Platinum (Pt) nanoparticles were prepared on TNTs by vapor-phase impregnation-decomposition method using platinum acetylacetonate [(CH<sub>3</sub>-COCHCO-CH<sub>3</sub>)<sub>2</sub>Pt] as precursor. Before the vapor impregnation step, TNTs and precursor powders were mechanically mixed in 3:1 weight ratio. To impregnate the TNTs with the precursor vapors, the mixed powders were heated at 453 K for 600 s inside a horizontal tube quartz reactor at a total pressure of 66.6 kPa. Then, the impregnated TNTs were moved to a higher temperature zone (673 K) inside the tube reactor to achieve the precursor decomposition. The crystal structure of the Pt/TNTs was investigated by X-ray diffraction (XRD) using Cu K $\alpha$  radiation in a Bruker D8 apparatus.

Scanning transmission electron microscopy (STEM) analysis was performed in a JEM-2200FS microscope with an accelerating voltage of 200 kV. The microscope is equipped with a Schottky-type field emission gun and an ultra high resolution (UHR) configuration (Cs = 0.5 mm; Cc = 1.1 mm; point to point resolution = 0.19 nm) and in-

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**Fig. 1.** Typical XRD patterns of (a) the TNTs obtained by the hydrothermal treatment and (b) the Pt/TNTs material.

column omega-type energy filter. The morphological images were obtained using the high angle annular dark field (HAADF) detector, which collects electrons that undergo Rutherford scattering. High resolution transmission electron microscopy (HRTEM) was performed in a Titan 80-300 microscope which operates at 300 kV of acceleration voltage and has a spherical aberration corrector in the TEM mode which gives a point to point resolution near a 0.1 nm. The samples were ground, suspended in isopropanol at room temperature, and dispersed with ultrasonic agitation. An aliquot of the solution was then dropped onto a 3 mm in diameter lacey carbon copper grid. Pt content in TNTs was determined by atomic absorption spectroscopy (AAS) with a Perkin-Elmer 2380 apparatus. Pt oxidation state and surface chemical composition was determined by X-ray photoelectron spectroscopy (XPS). The spectra were recorded on a THERMO-VG SCALAB 250 spectrometer equipped with Al K $\alpha$  X-ray source (1486.6 eV) and a hemispherical analyzer.

#### 3. Results and discussion

The Pt content determined by AAS was 14.5 wt%. Fig. 1 shows the typical XRD patterns of (a) the TNTs support obtained by the hydrothermal treatment and (b) the Pt/TNTs material. The angular Bragg positions of Pt fcc (JCPDS 04-0802) and TiO<sub>2</sub> tetragonal anatase phase (JCPDS 21-1272) are indicated as a reference. The XRD pattern of Fig. 1a exhibits low-intensity and broad reflections clearly located at different angular positions ( $2\theta = 11.96^{\circ}$ , 24.72° and 48.28°) from those of anatase phase, implying a different crystal structure which has been associated to the formation of TNTs by various research groups [20,21]. The small angle reflection at  $2\theta = 11.96^\circ$ , in particular, has been assigned to the distance between the walls of the nanotubes [22]. Various reflections from the Pt/TNTs material (Fig. 1b) correspond to those of anatase phase suggesting a collapse of the TNTs structure resulting from the incorporation of Pt at 673 K. This has been previously observed during the heat treatments of TNTs which cause a return to the anatase phase of the raw material used for the nanotube preparation [21]. However, it should be noted that the characteristic small angle reflection of TNTs remains even after the Pt deposition at 673 K, implying the coexistence of the anatase phase and TNTs structures. The asymmetric nature of the broad reflection at  $2\theta$  = 39.63° in Fig. 1b could be the result of the presence of Pt (111) at  $2\theta = 39.76^{\circ}$ .

Transmission electron microscopy analysis performed under HAADF-STEM mode revealed the presence of small white dots uniformly distributed on the titania nanotube. High density of white dots can be observed in HAADF image of Fig. 2. In this case, the white contrast was generated by the high intensity of the scattered electrons collected of the heavy atoms by the high angle annular detector where the intensity of the scattering electrons is directly proportional to the square of atomic number of the sample. Then, the small white dots were produced by Pt atom presence while the gray contrast was generated for the Ti and O atoms of the nanotube. Statistical analysis indicated that Pt nanoparticles have a size of about 2 nm.



**Fig. 2.** (a) TEM image of Pt/TNTs prepared by vapor-phase impregnationdecomposition method, (b) HAADF image of Pt nanoparticles distributed on the TNTs, and (c) particle size distribution of Pt/TNTs.

HRTEM analysis revealed that Pt nanoparticles were grown as small crystallites with a faceted morphology such as cubic or truncated octahedron (Fig. 3). A higher magnification of some Pt nanoparticles is illustrated in Fig. 4. The faceting of the small Pt particles is clearly appreciated. The *d*-spacing of 0.191 nm, 0.191 nm and 0.136 nm obtained by the Fourier transform (FT) well corresponded to the (200), (020) and (220) planes of the fcc crystal structure of Pt indicating a viewing direction parallel to the [001] direction of the Pt cubic structure. Then, the Pt particles show a surface face corresponding to the {200} planes with truncated edges associated to the {220} planes, marked by black arrows in Fig. 4a. The HRTEM image of the Pt nanoparticle shown in Fig. 4b displayed



Fig. 3. HRTEM image showing the crystalline arrangement of the small Pt nanoparticles.



**Fig. 4.** HRTEM image of single Pt nanoparticles. (a) Viewing direction parallel to [001] direction and its corresponding FT and (b) viewing direction parallel to [1-10] direction and its corresponding FT. Scale bar represent 1 nm.



**Fig. 5.** XPS spectra of (a) Pt 4f and (b) Ti 2p signals.

*d*-spacing of 0.222 nm, 0.221 nm and 0.191 nm which well corresponded to the (111), (1-1-1) and (002) planes, respectively, with a viewing direction parallel to the [1-10] direction. According with these data the Pt particle could be described as a truncated octahedron with  $\{111\}$  and  $\{002\}$  planes as the truncated surfaces, marked by white and black arrows, respectively.

Fig. 5a shows XPS details of the Pt 4f signal. After subtracting inelastic background, two doublets were necessary to fit the Pt 4f signal. The binding energy (BE) values were assigned to different oxidation states of Pt atoms according to literature data [23,24]. As shown in Fig. 5a, the peak at 70.5 eV was associated to the 4f 7/2 signal of metallic Pt (Pt<sup>0</sup>), with its corresponding 4f 5/2 peak at 73.9 eV, whereas the doublet with signals 4f 7/2 at 72.3 eV and 4f 5/2 at 75.7 eV was associated to oxidized Pt<sup>2+</sup> in PtO particles. The Pt<sup>0</sup>/Pt<sup>2+</sup> atomic ratio of 3.9 obtained in this study indicates that significant large amounts of Pt<sup>0</sup> were produced by vapor-phase impregnation-decomposition method on the surface of TNTs. Comparing with a wet impregnation method recently reported for Pt/TNTs [11] only 10% of Pt is reduced to Pt<sup>0</sup>, and about 90% of Pt remains in high oxidation Pt<sup>4+</sup> and Pt<sup>2+</sup> states. Then, the preparation method explored in this study represents a simple and high efficient growing procedure to obtain uniformly distributed Pt nanoparticles in a reduced oxidation state on the surface of TNTs. Two doublets were also necessary to fit the Ti 2p signal in the XPS spectrum shown in Fig. 5b. The BE value reported for  $Ti^{4+} 2p_{3/2}$  is 458.5 eV. This peak shifts to lower energies when the valence state of Ti<sup>4+</sup> is reduced to Ti<sup>3+</sup> [25]. In this case, one of the peaks  $2p_{3/2}$  is about 458.5 eV and the other is about 457.5 corresponding to Ti<sup>4+</sup> and Ti<sup>3+</sup>, respectively. The surface atomic ratio of Ti<sup>3+</sup>/Ti<sup>4+</sup> was 0.4 suggesting that the noble metal impregnation induce the partial reduction of a considerable amount of Ti atoms.

## 4. Conclusions

Pt nanoparticles were prepared on TNTs by the vapor-phase impregnation-decomposition method. This method proved to be successful to incorporate homogeneously distributed Pt nanoparticles on the surface of TNTs with a narrow distribution of particle size (2.1 nm mean particle size). Pt nanoparticles remain mainly as Pt<sup>0</sup> oxidation state with a Pt<sup>0</sup>/Pt<sup>2+</sup> atomic ratio of 3.9.

## Acknowledgments

The authors would like to acknowledge the IPN and IMP for the financial support through the projects: IPN-SIP 20080927 and IMP-D.00446. One of the authors (C. Encarnacion) is grateful to CONACYT for the scholarship for graduate studies.

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