

WO_x nanoclusters highly dispersed on titania nanofibers

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WO_x-TiO₂ catalysts with different W contents on titanium oxide nanofibers were prepared by impregnation of (NH₄)₂WO₄ aqueous solution and annealed in air at 400 °C. X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM), high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and Raman spectroscopy were used for chemical and structural characterization. The results revealed that the support consisted of β-titanium oxide nanofibers with WO_x species highly dispersed on the nanofibers saturating the surface at a concentration around 30 wt%. With an increase in the W concentration to 40 and 50 wt%, a crystalline WO₃ phase segregates from the support, growing as large WO₃ crystallites, whereas the support remains homogeneously decorated by WO_x nanoclusters with dimensions around 1.0 nm. The W atoms remained octahedrally coordinated with a W=O Raman vibrating band at 974 cm⁻¹.

Key Words: Tungsten Oxide, TiO₂, Catalyst, Nanofibers, HRTEM, HAADF-STEM, Raman Spectroscopy.

Introduction

Nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures. Currently, this is an area of intense scientific research, due to a wide variety of potential applications in several fields. The main characteristic of nanomaterials is the increase surface/bulk atomic ratio opening new possibilities in surface-based science, such as catalysis. A number of physical phenomena become noticeably pronounced as the size of the system decreases. These include statistical mechanical effects, as well as quantum mechanical effects, for example the “quantum size effect” where the electronic properties of solids are modified with great reductions in particle size [1]. Such characteristics are strongly used in catalytic systems where the more studied components have been Au [2, 3], Pt [4], Pd [5], W [6] etc, supported on Al₂O₃, SiO₂, TiO₂ and ZrO₂, mainly. Each catalytic system presents particular characteristics and its properties must first be understood.

Tungsten oxide is used to catalyze several chemical reactions such as alcohol dehydrogenation, n-alkane isomerization, oxidative desulfurization, cracking and alkylation of hydrocarbons due to the high acidity that the catalyst presents when WO_x is supported on alumina, zirconia or titania [7-9]. WO_x-ZrO₂ is one of the most studied systems and it has been established that WO_x active species are obtained above 700 °C if the zirconia structure is mainly in its tetragonal phase [10]. However, results reported more recently give evidence that the

WO_x species can be obtained from 400 °C on a TiO₂ support [11]. This system presents no structural problems as in the case of zirconia. A disadvantage with titania is its specific surface area which may be improved by changing its morphology, generally as nanotubes or nanofibers [12] reporting a surface area around of 348 m²/g. More detailed results about the behavior of the WO_x species on titania nanotubes with temperature, reported that the nanotubular morphology collapsed in anatase nanoparticles at 500 °C and the specific surface decreased to around 70 m²/g. However, recently it has been found that titanium oxide nanotubes were partially transformed into anatase after annealing in air at 400 °C and maintained their nanotubular morphology [13]. Then, the thermal stability of the nanotubes is suitable for chemical reactions taking place below 400 °C but not for higher temperature. Therefore it is very important to produce a support with high thermal stability at high temperature that does not change with W impregnation and can be activated a low temperature.

In this study, highly dispersed WO_x nanoclusters on titania nanofibers as WO_x-TiO₂ catalyst were prepared by impregnation of TiO₂ nanofibers with an ammonium metatungstate solution. The dispersion and size of the WO_x species was determined mainly by HAADF-STEM analysis and Raman spectroscopy.

Experimental

Synthesis of materials

Titanium oxide nanofibers were synthesized by alkali hydrothermal treatment of an anatase precursor with a crystallite size of 8.0 nm following the procedure published elsewhere [13] at 140 °C. The starting support with a nanofiber morphology, dried at 100 °C had specific surface

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area (SSA) of 270 m²/g, a pore volume of 0.61 and a pore diameter of 6.3 nm. 22 g of the support was impregnated with 200 cm³ of an ammonium metatungstate solution at variable concentrations in order to obtain 30, 40, 50 wt% of W on the final product. Samples were identified as NFW30, NFW40 and NFW50, respectively. The pH of the solution was adjusted to 10 with a few drops of ammonium hydroxide. The slurry was aged 1 h at room temperature, and then excess water was eliminated by evaporation at 100 °C, heated by an oil bath in a rotary evaporator. Finally, samples were dried overnight at 110 °C, and then calcined at 400 °C in air flow for 4 h.

Characterization techniques

X-ray diffraction (XRD) patterns of the samples, packed in a glass holder, were recorded at room temperature with Cu K_α radiation in a Bruker Advance D-8 diffractometer having a theta-theta configuration and a graphite secondary-beam monochromator. Diffraction intensity was measured in the 2θ range between 5 and 80°, with a 2θ step of 0.02° for 8 s per point.

Textural properties were determined in an ASAP-2000 analyzer from Micromeritics. SSA was calculated from the Brunauer-Emmet-Teller (BET) equation from N₂ physisorption at 77 K. The pore size distribution was obtained by the Barrett-Joyner-Halenda method in the desorption stage. Dried samples were outgassed at 373 K and those calcined at 673 K were outgassed at 623 K.

Raman spectra were obtained using an Yvon Jobin Horiba (T64000) spectrometer, equipped with a CCD camera detector. As a source of excitation, the 514 nm lines of a Spectra Physics 2018 Argon/Krypton Ion Laser system were focused through an Olympus BX41 microscope equipped with a 50x magnification objective. The laser power never exceeded 5 mW on the sample.

High resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM) analysis were performed in a JEM-2200FS transmission electron microscope with an accelerating voltage of 200 kV. The microscope was 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 an in-column omega-type energy filter. As STEM is particularly useful in studies of nanoparticles using a high angle annular dark field (HAADF) detector which collects electrons that undergo Rutherford scattering, images can be acquired where the intensity is approximately proportional to Z² [14] (Z is the atomic number of the scattering atom). Therefore, elements with a high Z produce a higher intensity and white contrast images. The technique is useful to disclose the presence of different chemical elements when there is a big difference in their atomic numbers, such as those in supported catalysts. Local chemical analysis by energy dispersive X-ray spectrometry (EDXS) was performed in a NORAN energy dispersive X-ray spectroscopy, which was attached to the microscope, using the STEM-EDX

Table 1. Textural properties of the samples loaded with different W concentrations after annealing at 400 °C

Sample	SSA (m ² /g)	Mean Pore Volume (cm ³ /g)	Mean Pore diameter (nm)	W Nominal wt. %
NF	195	0.44	6.3	0
NFW30	107	0.27	8.3	30
NFW40	93	0.22	7.7	40
NFW50	100	0.24	8.0	50

combination. The samples were ground, suspended in 2-propanol at room temperature, and dispersed with ultrasonic agitation; then, a drop of the solution was placed on a 3 mm diameter holey carbon copper grid.

Results and Discussion

Textural properties of all W impregnated samples and subsequently calcined at 400 °C are reported in Table 1. SSA of the impregnated samples decreased from 270 to around 100 m²/g while the sample without impregnation and annealed to the same temperature only decreased to 195 m²/g. This considerable SSA decrease of the impregnated samples is attributed to the impregnation of nonporous and heavy entities, WO_x. A similar behavior was obtained with the mean pore volume and mean pore diameter.

Bright field transmission electron microscopy (TEM) image shows clearly that the TiO₂ support was conformed basically of nanofibers, Fig. 1. The external diameter distribution was broad, between 30 and 100 nm, with several micrometers in length although some short nanofibers were also observed. From the TEM results,

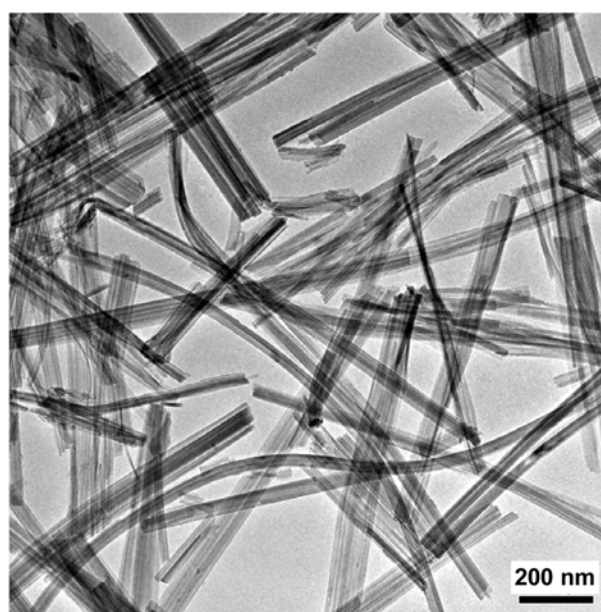


Fig. 1. Bright field TEM image of the support evidencing the TiO₂ nanofiber morphology.

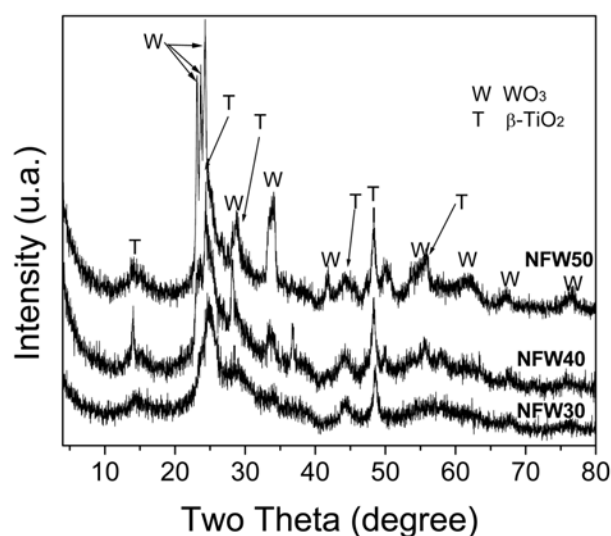


Fig. 2. XRD patterns of the samples impregnated with different W loads.

the mean pore diameter obtained by BET is related mainly with the void space generated by the intertwining of the nanofibers.

XRD results indicate that support was composed basically by the β -titanium oxide phase (JCPDS card number 46-1238), Fig. 2. As can be seen, the sample that had a W load of 30 wt%, an absence of diffraction peaks corresponding to a different phase to the crystalline structure of the TiO_2 support was observed, XRD pattern named as NFW30. Therefore, the result is indirectly indicating a high dispersion of WO_x species on the nanofibers. At higher W loadings, XRD patterns corresponding to the NFW40 and NFW50 samples clearly showed the characteristic diffraction lines of the WO_3 phase according to the JCPDS card number 20-1324. The presence of

the WO_3 diffraction peaks together with the β -titanium oxide diffraction peaks in the same XRD pattern gives strong evidence of the segregation of the WO_3 phase from the nanofibers, suggesting that its surface has been saturated by WO_x nanoclusters at 30 wt% of W.

The WO_x dispersion on the nanofibers was studied by TEM. The morphology of the β -titanium oxide nanofibers after the impregnation process and annealing at 400°C was not modified obtaining similar results to the illustrated in Fig. 1. At low magnifications, the TEM images not evidenced the presence of WO_x species on the nanofibers indicating a high WO_x dispersion of nanometric size. Is important to notice that the TEM is a local form of analysis and therefore, WO_3 particles was not possible to evidence in the analyzed regions of the samples with a high W load. At higher magnifications, HRTEM image of Fig. 3, small dark dots were observed on the nanofibers. These were produced for the heavy atom accumulation such as the W atoms or WO_x clusters, more clearly shown Inset A Fig. 3. The presence of these heavy atom clusters on the nanofibers was much better evidenced by obtaining images with the electrons dispersed at high angle. These electrons have information about the chemical composition because the intensity after crossing the sample is directly proportional to the square of the atomic number of the atoms present in the sample. So, the heavy atoms will give a more intense signal and will produce a whiter contrast than the generated by lighter atoms in a dark field image in the STEM mode. Figure 4 shows a typical HAADF-STEM image of the impregnated samples. Small white dots uniformly covering the β -titanium oxide nanofibers are observed. These white dots represent WO_x clusters because the W atoms scatter about 10 times more than Ti atoms in a HAADF-STEM image due to

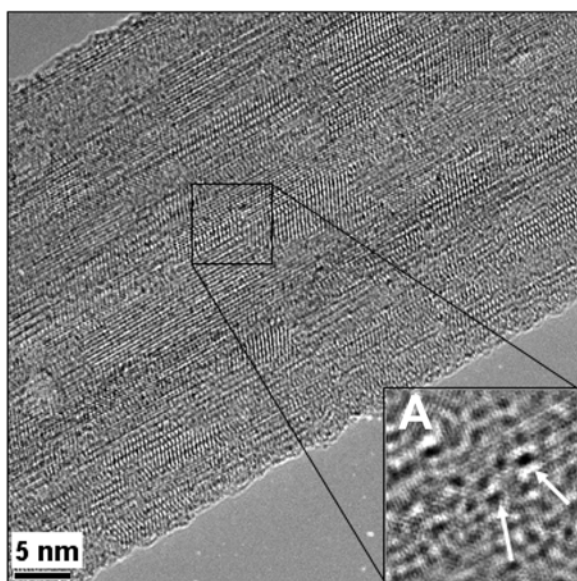


Fig. 3. HRTEM image of a nanofiber showing small dark dots produced by heavy atom accumulations. Inset A higher magnification.

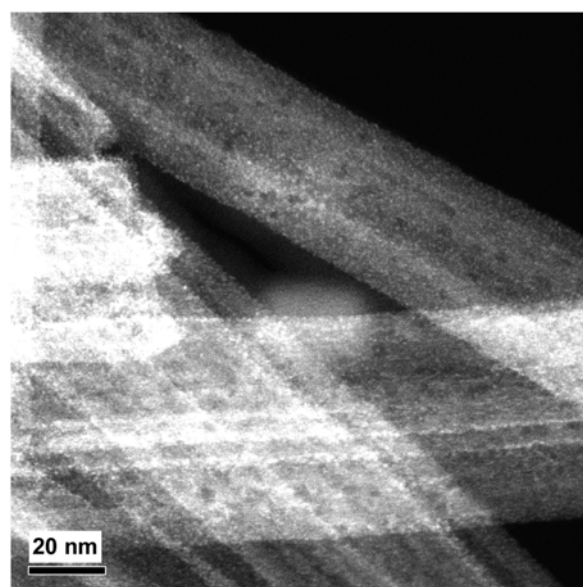


Fig. 4. HAADF-STEM image showing small white dots uniformly dispersed on the nanofibers. The white contrast was produced by the presence of tungsten atoms.

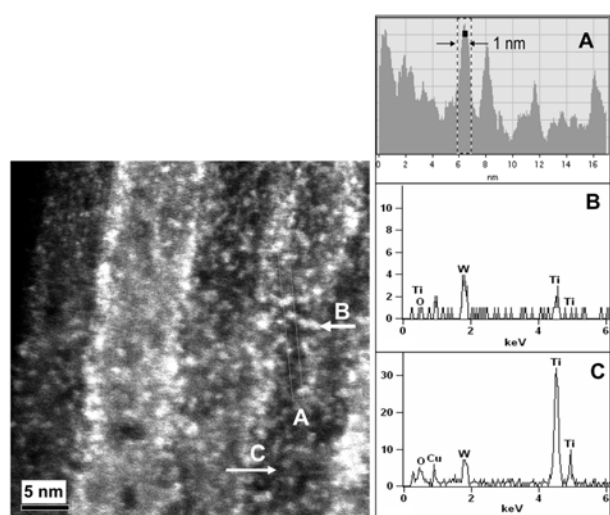


Fig. 5. HAADF-STEM image showing the nature of W atoms cluster. Inset A intensity profile revealing the size of the clusters. Inset B EDX spectrum of the white dots and Inset C EDX spectrum of the support.

the difference of atomic number between the W atom ($Z = 74$) and the Ti atom ($Z = 22$). The result strongly evidences the high WO_x dispersion on the surface of the nanofibers. A more detailed HAADF-STEM image, Fig. 5, shows more clearly the nature of these atom clusters. The WO_x species have different shape and sizes generally less than or equal to 1.0 nm such as it is illustrated in the intensity profile taken from a line drawn in the HAADF-STEM image, Inset A. Local chemical analysis performed in the white dots confirmed the presence of W atoms, mainly. A high intensity in the W peak in the EDX spectrum was detected, Inset B, while in the areas where there were no white dots Ti atoms were more strongly detected, Inset C. EDXS chemical analysis confirmed very well the HRTEM and HAADF-STEM results. Similar results were obtained for all impregnated samples.

Raman spectra of the samples with different W load and annealed at 400 °C including the W free support are plotted in Fig. 6. The Raman spectrum of the dry titania nanofibers display mainly four characteristic bands at 195, 272, 448 and 667 cm⁻¹ according to the literature [15]. As can be seen in the spectrum named as NF, bands corresponding to the anatase phase were not detected. The active modes of the anatase phase are 144, 200, 400, 505, 640 and 796 cm⁻¹. Notwithstanding, the exact assignment of the bands in the Raman spectra of TiO₂ nanofibers is still a matter of debate. Accordingly, the bands at 450 and 668 cm⁻¹ could be assigned to Ti-O-Ti vibrations [16]. Additionally, displacements of the bands in the Raman spectra were obtained with an increase of W on the support. However a band was localized at 974 cm⁻¹ which was attributed to symmetric vibration of W = O bonds in the octahedral coordination [15, 17]. The same position was observed in the samples with 40 and 50 wt% W. In the sample with 50 wt% W, in addition to the vibration at 974 cm⁻¹ another vibration at 792 cm⁻¹ was detected.

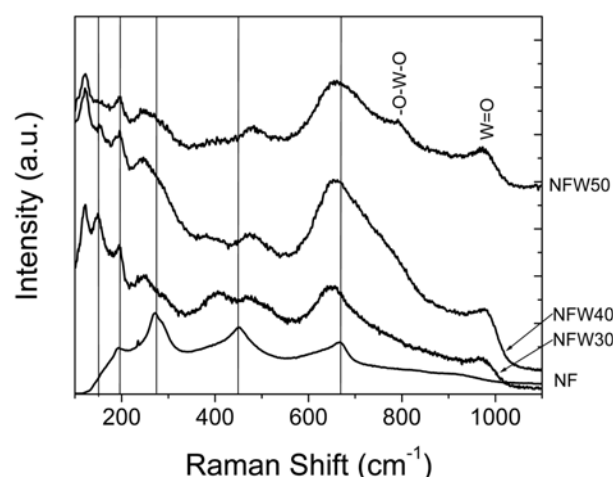


Fig. 6. Raman spectra of the samples with different W contents.

According to the literature [18] this vibration is attributed to the W-O stretching mode indicating the existence of crystalline WO₃ which is in good agreement with the XRD results. According to the Raman results, the small white dots seen in the HAADF-STEM image which were rich in W and deposited on the nanofibers, remained in an octahedral coordination with nanosize dimensions below 1 nm. Nanoclusters larger than 1 nm were not observed in the samples with a high W content. When the surface was saturated with tungsten oxide nanoclusters, larger WO₃ crystallites segregate. It is interesting remark that the WO_x nanoclusters no enlarge its size on the nanofiber surfaces, they segregate as larger crystallites producing two separated phases: β -TiO₂ smeared with WO_x nanoclusters and larger WO₃ particles.

Conclusions

Highly dispersed tungsten oxide nanoclusters with dimensions smaller than 1 nm deposited on the β -titanium oxide nanofibers were obtained. The maximum W load on the support was around 30 wt%, more W load crystalline WO₃ phase is segregated. The tungsten oxide was deposited on the nanofibers with an octahedral coordination and the maximum size that the WO_x cluster could be deposited on the surface is around 1 nm.

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