Characterization by TEM of Pt nanoparticles dispersed on TiO$_2$Np, TiO$_2$Nt and Al$_2$O$_3$

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The development of new catalysts for hydrogenation and dehydrogenation, isomerization, oxidation reactions using metals as active phase are reducing the metallic load at concentrations smaller than 1 wt.%. Therefore, information about the dispersion, size and chemical composition of the metallic phase is fundamental to understand the selectivity, reactivity and conversion results of the new catalytic formulation. Here, transmission electron microscopy plays an important role in the catalysis field [1]. This instrument gives information about the chemical composition, size and crystalline structure to a nanometric scale.

Pt catalysts are widely used in hydrogenation reactions. Mechanisms to improve the metallic dispersion at concentrations smaller than 1 wt.% is currently being investigated [2]. In this work, we present results about the dispersion, size and morphology of Pt dispersed on TiO$_2$ nanoparticles (TiO$_2$Np), TiO$_2$ nanotubes (TiO$_2$Nt) and Al$_2$O$_3$ nanoparticles. The samples were impregnated with platinum bis-acetylacetonate. Subsequently, these were reduced in an H$_2$ stream by heating at 350°C. The total percentage of platinum on the support was 1.0 wt.%. A transmission electron microscope JEM2200 FS, which operated at 200kV, was used in order to evidence the Pt dispersion on the supports. Annular dark field (ADF) images in the scanning transmission electron microscopy (STEM) mode were acquired. Chemical analysis was performed with an energy dispersive X-ray (EDX) spectrometer Noran attached to the microscope. The samples were dispersed in isopropanol using ultrasonic stir. Subsequently, an aliquot was put on a cooper grid of 200 mesh covered with a polymeric film.

ADF-STEM images obtained from each sample show brighter dots dispersed on the supports, see figure 1. Qualitatively, the size of these bright dots were smaller in TiO$_2$Np sample than TiO$_2$Nt and Al$_2$O$_3$ samples. Therefore, this result suggests that the active phase was better dispersed on TiO$_2$Np. Quantitatively, the average size of particle was determined by a statistical analysis of 158, 205 and 146 bright dots for the TiO$_2$Np, TiO$_2$Nt and Al$_2$O$_3$ samples, respectively. The particle average size calculated was 0.9±0.1 nm, 3.0±0.4 nm and 2.3±0.3 nm for the TiO$_2$Np, TiO$_2$Nt and Al$_2$O$_3$ samples, respectively. Clearly can be appreciated a particle size most homogeneous in the TiO$_2$Np sample.

Chemical analysis performed by EDX spectroscopy on brighter dots revealed characteristic peaks presence corresponding to the Pt-M and Pt-L energy shell on the three samples, see EDX spectra of figure 2. Therefore, the brighter dots observed in the ADF-STEM images were generated from electron scattered by the cores of the Pt atoms. These Pt nanoparticles were on the surface of the particles used as support such as is evidenced by each one of the characteristic peaks present in the EDX spectra. O and Ti for TiO$_2$Np and TiO$_2$Nt and O and Al for Al$_2$O$_3$. Cu peaks correspond to the grid cooper. Each EDX spectrum shows the chemical nature of the bright dot and their surroundings.

The atomic resolution images of the brighter dots was obtained. The atomic lattice shows a hexagonal geometric arrangement indicating that these Pt nanoparticles were oriented along the [110] direction.

This bidimensional projection correspond to a cuboctahedral Pt model, which has been reported as a typical growth of metallic Pt at the nanometric scale. From these results, the best Pt dispersion was obtained in the TiO₂Np sample.

References:

[1] L Delannoy, *et al*, Phys.Chem.Chem. Phys., **15**, 2013, 3473-3479.
[2] JS King, *et al*, Nano Lett., **8**, 2008, 2405-2409.
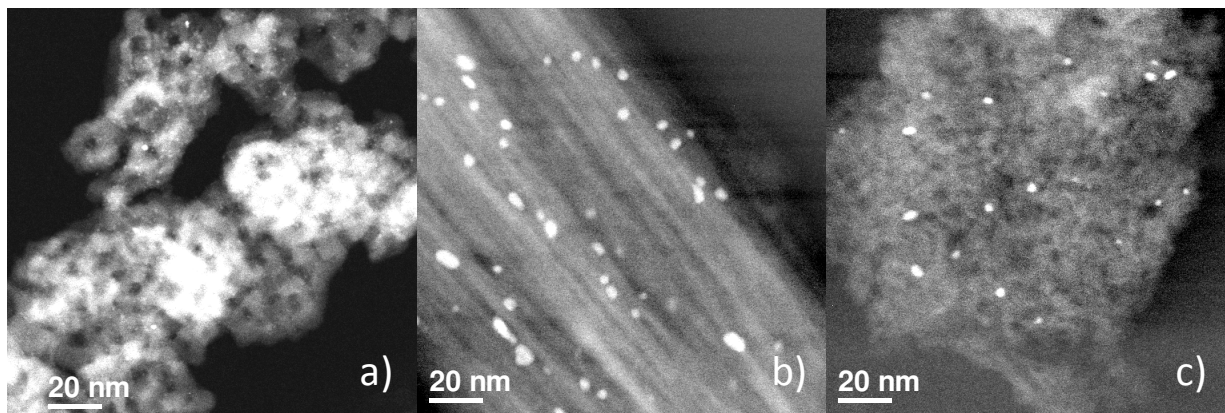[3] The authors acknowledge financial support to IMP through project D.00447.

Figure 1. ADF-STEM images showing bright dots highly dispersed on a) anatase TiO₂ nanoparticles, b) TiO₂ nanotubes and c) Al₂O₃ nanoparticles.
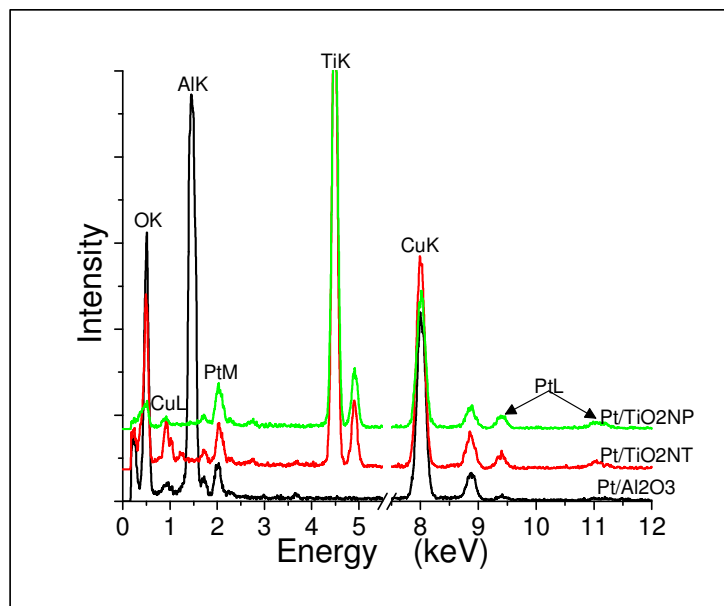

Figure 2. EDX spectra obtained from a single bright dot deposited on the different supports. Peaks of the L and M characteristic energy shells of the platinum were clearly revealed in the spectra.