

Structural Analysis of HR-TEM Images of Ni-doped Zirconia Nanoparticles

C. Angeles-Chavez*, D. A. Prado-Chay, M. A. Cortes-Jacome, J.A. Antonio-Toledo.

Gerencia de Desarrollo de Materiales y Productos Quimicos, Instituto Mexicano del Petroleo, Eje Central Lazaro Cardenas No 152, C.P. 07730, Ciudad de Mexico, MEXICO.

*Corresponding author: cangeles@imp.mx.

Zirconia has high thermal stability, low thermal conductivity, and high resistance to corrosion. Therefore, it is used as refractory materials, pigments, piezoelectric devices, ceramic capacitors, oxygen sensors, and as catalysts, among other uses [1]. Zirconia in pure form, exhibits three well-defined polymorphs. At room temperature, it has a monoclinic structure, at 1170°C is tetragonal and after 2370°C, the structure is cubic [2]. The *m*-ZrO₂/*t*-ZrO₂ transformation is thermodynamically reversible while the *c*-ZrO₂ is only thermodynamically stable at temperatures above 2370 °C [3]. However, the addition of certain aliovalent oxides can stabilize the *t*-ZrO and *c*-ZrO₂ structures at room temperature. Between these aliovalent oxides, the NiO has been found to be a good candidate for the stabilization of both structures.

On the other hand, the Ni-ZrO₂ system is very important because can be used as catalyst in the partial oxidation of methane into higher hydrocarbons. Previous works have evidenced that Zr⁴⁺ ions were found to substitute Ni²⁺ ions in the NiO lattice forming a ZrO₂-NiO solid solution [4]. This produces strong interaction between Zr and Ni atoms decreasing the NiO reducibility and modifying the nature of oxygen species adsorbed, which plays an important role in the catalytic performance. Therefore, gain insight about the crystalline structure of Ni-doped ZrO₂ nanoparticles is important in order to improve the new synthesis routes with a better catalytic performance.

Ni-Zr-O samples were prepared through the co-precipitation technique using Zr-salt (ZrOCl₂·8H₂O) and Ni-salt (NiCl₂·6H₂O). NH₄OH was used as precipitating agent. The precursor quantities were adjusted to obtain Ni-Zr-O samples of 0, 2, 5, 7 and 10 wt.% Ni and named Ni-0, Ni-2, Ni-5 and Ni-10, respectively. All samples were calcined at 600 °C. Elemental chemical composition and structural characterization were performed by SEM-EDX (FEI Nova NanoLab DualBeam, EDAX) and HR-TEM (JEM-2200FS).

The elemental chemical composition results revealed the presence of Ni atoms in all samples and was very close to the nominal: 0, 3.0, 5.8, 7.6 and 9.6 wt.% Ni, respectively. Single nanoparticles were not resolved by SEM analysis suggesting that the synthesis method generated Ni-Zr-O nanoparticles in the nanometric scale. Around 10 nm according to TEM analysis. TEM-EDX results evidenced presence of Ni atoms in the Ni-Zr-O nanoparticles, see EDX spectrum illustrated in Fig. 1 of the Ni-0 and Ni-10 samples. NiK line is clearly appreciated in the EDX spectrum of the Ni-10 sample. The Cu peaks correspond to the Cu grid. Structural analysis of the HR-TEM images of the single nanoparticles of the Ni-0 sample matched very well with the *m*-ZrO₂ structure while in the Ni-2 sample, the nanoparticles were adjusted to a *t*-ZrO₂ structure JCPDS card 50-1089, see nanoparticle of Fig. 2a and Fourier spectrum of Fig. 2b. The Fourier spectra of the atomic resolution images of the nanoparticles in the Ni-3, Ni-5 and Ni-7 samples were indexed with the structure of the *c*-ZrO₂ JCPDS card 49-1642. Figures 2c and 2d show results of a single nanoparticle of the Ni-5 sample. The same ZrO₂ structure was identified in the nanoparticles of the Ni-10 sample. A single nanoparticle is illustrated in Fig. 3, letter B. In this sample, smaller nanoparticles segregated on the *c*-ZrO₂ nanoparticles were observed as illustrated in Fig.

3, letter A. Their Fourier spectrum fitted to the *c*-NiO structure JCPDS card 47-1049. Therefore, *c*-NiO nanoparticles co-existing with *c*-ZrO₂ nanoparticles to 9.6 wt.% Ni was obtained. These preliminary results could suggest saturation of Ni atoms into the lattice of *c*-ZrO₂ structure from 7 wt.% Ni in the NiO-ZrO₂ system when is synthesized by the co-precipitation method.

References:

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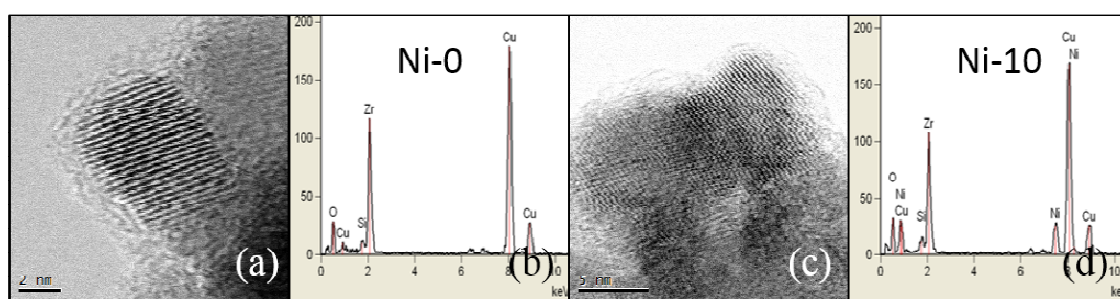


Figure 1. HR-TEM images of single nanoparticles of the a)Ni-0 and c)Ni-10 samples and b) and d) their punctual EDX spectra, respectively.

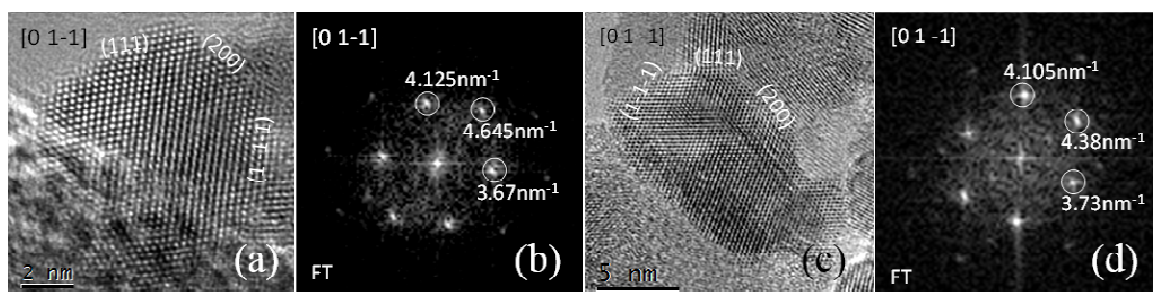


Figure 2. HR-TEM images of single nanoparticles of the a)Ni-2 and c)Ni-5 samples and b) and d) their corresponding Fourier spectra.

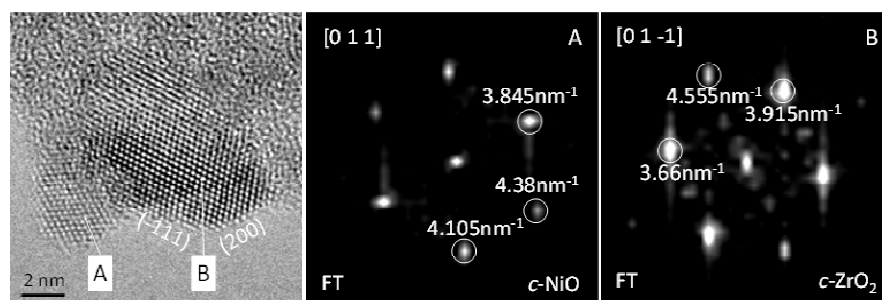


Figure 3. HR-TEM image of nanoparticles of the Ni-10 sample. The Fourier spectra A and B correspond to nanoparticles marked by A and B in HR-TEM image.