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Structural characterization by HRTEM of WO_x nanocluster obtained from W-ZrO_2 solid solution

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Tungsten oxide dispersed on zirconia in WO_3-ZrO_2 system seems to be the more stable catalyst with strongly acidic properties. The activation of the catalytic sites depends on synthesis method. It has been assumed that for impregnated catalysts all tungsten is on crystallite surface, whereas in coprecipitated and sol gel synthesis methods WO_3 crystallites remain in ZrO_2 bulk, stabilizing the tetragonal structure [1,2]. Recently we reported the formation of the solid solution W-ZrO_2 occurring below 800 °C, which stabilizes the tetragonal structure in a highly symmetric state producing crystallites with flat surfaces[3]. Upon 800 °C, the tungsten atoms segregate from the tetragonal solid solution, producing the monoclinic and tetragonal phases of zirconia. It seems that the segregation process of tungsten atoms from the solid solution controls the aggregation of the WO_x species on the zirconia crystallites surface. In this work experimental evidence of the segregation and well dispersed WO_3 on ZrO_2 surface was obtained by using high-resolution transmission electron microscopy HRTEM (JEOL 2010F).

The sample was prepared from aqueous solution of oxynitrate and ammonium metatungstate hydrate and precipitated at constant pH (9.5-10). The obtained white slurry was aged for 24 h at room temperature. Then, it was filtered and dried at 110°C in vacuum for 18 h; dried powders were annealed at 560 and 800 °C for 4 h, in flowing air.

The X-ray diffraction pattern of the sample annealed at 560 °C was best adjusted by modeling it with two tetragonal phases, denominate T1 and T2. The crystallite size obtained for the Rietveld refinement of these two tetragonal phases was 6.3(2) and 44(3) nm for T1 and T2, respectively. The concentration was of 59 wt % of T1 and 41 wt % for T2 phase. Two different crystallite sizes were obtained by TEM confirming the XRD and Rietveld results. The T1 phase had a spherical morphology while T2 phase had irregular shape. Both were characterized as tetragonal ZrO_2 phase. On the other hand, the T2 phase presented many structural imperfections, figure 1. The squares A show border- type dislocations and the square B shows a point defect. These structural defects were produced by the high W atom concentration present in those regions. The T1 phase not showed these crystalline defect types. The results suggest that the T2 phase was richer in W atoms than the T1 phase. Therefore, when the sample was annealed at 800 °C, the T2 phase segregated the W atoms dissolved into its lattice, and it was transformed into monoclinic phase. The concentration of T1 phase did not changed, only grew its crystallite size from 6.3(2) to 23.2(4) nm. The TEM results confirmed the presence of the tetragonal and monoclinic ZrO_2 phases. Both phases were decorated by WOx nanocluster, such as is illustrated in figure 2a, yielding a rough surface. The WOx nanoclusters sizes (0.5-1.0 nm) on the T1 phase, however, were smaller than the WOx nanoclusters of the monoclinic zirconia phase (1.0-2.0 nm). In figure 2b is illustrated a HRTEM image corresponding to a crystal of monoclinic ZrO_2 phase. A nanocluster emerged from the crystal and it is deposited on its surface, which was identified as orthorhombic WO_3 phase viewed in the [1 -1 0] direction. Therefore, the nanoparticles segregated on the crystallite surface correspond to the orthorhombic WO_3 phase.

References

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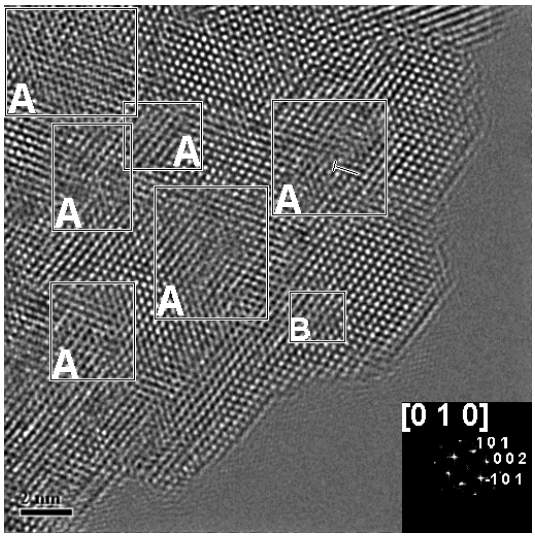

Fig. 1.) HRTEM micrograph of the tetragonal T2 phase at 560 ºC viewed in the [2 -2 1] direction. Inset FFT pattern.

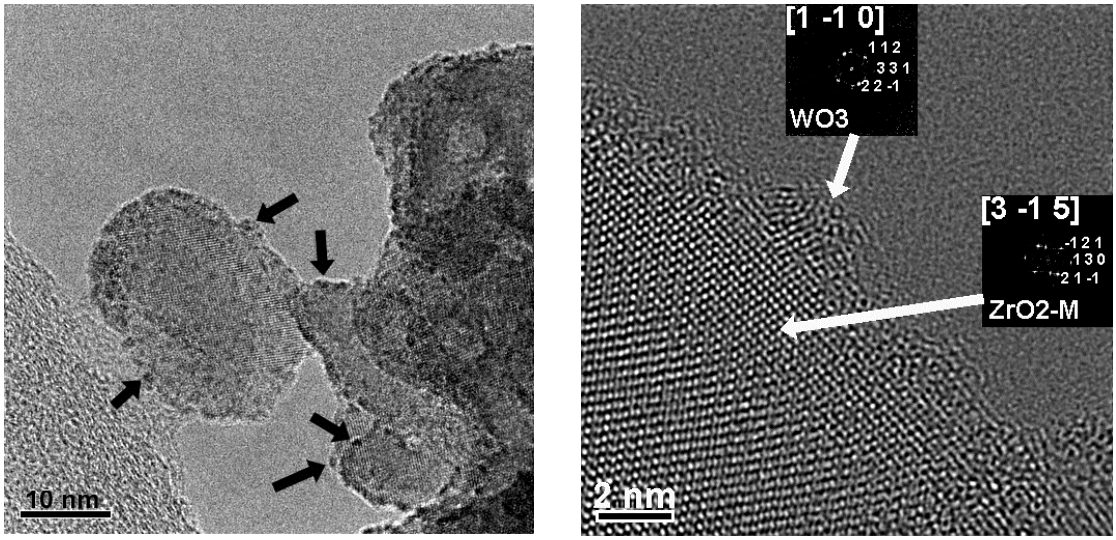

Fig. 2. a) TEM micrograph of the sample annealed at 800 °C showing dark WOx nanocluster on the crystallite surface. b) HRTEM micrograph of a monoclinic ZrO_2 crystallite viewed in the [3 -1 5] direction and a nanoclusters of orthorhombic WO_3 viewed in the [1 -1 0] direction. Inset FFT patterns.

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