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Generation of WO_3–ZrO_2 catalysts from solid solutions of tungsten in zirconia

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Abstract

WO_3–ZrO_2 samples were obtained by precipitating zirconium oxynitrate in presence of $WO_4^{=}$ species in solution from ammonium metatungstate at pH = 10.0. Samples were characterized by atomic absorption spectroscopy, thermal analysis, X-ray diffraction, Raman spectroscopy, X-ray photoelectron spectroscopy, high-resolution transmission electron microscopy and energy filtered-TEM. The ammonia retained in the dried sample produced a reductive atmosphere to generate W^{5+} ions coexisting with W^{6+} ions to produce a solid solution of tungsten in the zirconia lattice to stabilize the zirconia tetragonal phase when the sample was annealed at 560 °C. When the sample was annealed at 800 °C, the W atoms near crystallite surface were oxidized to W^{6+}, producing patches of WO_3 on the zirconia crystallite. The HR-TEM analysis confirmed the existence of the solid solution when the sample was annealed at 560 °C, and two types of crystalline regions were identified: One with nearly spherical morphology, an average diameter of 8 nm and the atomic distribution of tetragonal zirconia. The second one had a non-spherical morphology with well-faceted faces and dimensions larger than 30 nm, and the atom distribution of tetragonal zirconia. When samples were annealed at 800 °C two different zirconia crystallites were formed: Those where only part of the dissolved tungsten atoms segregated to crystallite surface producing patches of nanocrystalline WO_3 on the crystallite surface of tetragonal zirconia stabilized with tungsten. The second type corresponded to monoclinic zirconia crystallites with patches of nanocrystalline WO_3 on their surface. The tungsten segregation gave rise to the WO_3–ZrO_2 catalysts.

Keywords: Tungsten zirconia catalysts; Solid solutions; Tetragonal zirconia; XPS; Raman spectroscopy; HR-TEM; EFTEM

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1. Introduction

Solid catalysts with strong acidity play an important role in hydrocarbon conversion reactions; for example, in isomerization and alkylation processes [1–4], which involve reactions of great interest in the production of the additives that enhance gasoline octane. Halogen-promoted metal oxides (e.g., chlorinated alumina), liquid acids and strong liquid acids supported onto a porous matrix are the catalysts commercially available for the above applications. These catalysts, however, are unstable, deactivate quickly, and produce corrosive gases with the consequent damage of installations and environment [5–7].

Zirconia modified with sulfate [8], phosphate [9], heteropolyacids HPA [10], tungsten [11], and molybdenum [12] has emerged as an alternative catalysts to substitute chlorinated alumina and liquid acids catalysts. These zirconia based catalysts can be regenerated easily and contain a metal as promoter that generates strong solid acid catalysts able to isomerize n-butane near room temperature [13–15]. From them, tungsten oxide dispersed on zirconia seems to be the most stable and is characterized by having a strong acid sites density [13].

The activation of the catalytic sites depends on synthesis method, where the annealing temperature plays a special role. When coprecipitation [11] and sol–gel [16] methods are used for the synthesis, the samples require higher annealing temperatures for activation than those prepared by impregnation in hydrous zirconia [17]. When these catalysts are prepared by impregnation, all tungsten is on

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crystallite surface, whereas in coprecipitated and sol–gel synthesis methods it is assumed that W atoms incorporate into ZrO_2 lattice, stabilizing the tetragonal structure [11,16]. Both synthesis methods require high temperatures to have tungsten oxide on zirconia crystallites surface. Because tungstate species entrapped in the bulk of the zirconia must be expelled onto the surface [16–18], little attention has been paid to explain how the W atoms remain in the ZrO_2 lattice stabilizing the tetragonal structure. Zirconia surface stabilization mechanism by oxoanions such as, tungstate, molybdate, or sulfate, is to date, the most accepted hypothesis, establishing coverage of WO_x species of a ZrO_2 core. These WO_x species have been postulated on basis of the local environment around the W atoms, where the oxygen coordination numbers assume values of 4 for a tetrahedral and 6 for an octahedral coordination. The possibility of the W atoms reduction to form solid solution with ZrO_2 at low temperature has not been yet considered, this subject will be addressed in this work.

Recently we reported that tungsten and zirconia oxide form solid solutions below 800 °C, stabilizing zirconia in two tetragonal crystalline phases [20] that differ mainly in the oxygen position along the *c*-axis. In the phase with higher symmetry this position is at 0.50(2), producing flat crystallite surfaces perpendicular to the *c*-axis, while in the phase with the lower symmetry it is at 0.447(2), giving rise to rough crystallite surfaces parallel to (100) planes. When the sample is annealed at 800 °C its acid site density is two times higher than when it is prepared by impregnation [11]; it seems that the segregation of tungsten atoms from the crystallite bulk to its surface determines the WO_x species on it.

In the literature it is assumed that the high acid site density obtained in the zirconia system after calcining samples above 850 °C is due to the coverage of crystallites surface with a monolayer of WO_3 [13,16,21]. When tungsten content is higher than the ideal amount to produce only one monolayer, it gives rise to three-dimensional WO_x species [21] that produce a higher isomerization activity than the ones formed in the WO_x/Al_2O_3 system [22]. The preparation techniques used are devoted specially for designing microstructure of WO_x species on the surface of ZrO_2, which is thought to be useful for catalysis. The possibility of formation of solid solution $(WZr)O_2$ at certain stage of the preparative treatment procedure has been scarcely considered in the literature.

In the present work, the thermal evolution of crystalline phases generated in the WO_3–ZrO_2 system was analyzed by using, thermal analysis (TGA-DTA), X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectronic spectroscopy (XPS), Energy filtered transmission electron microscopy (EFTEM), high resolution transmission electron microscopy (HR-TEM) and X-ray energy dispersive spectroscopy (EDS), which complement our previous study on the system made with X-ray diffraction and refinement of the crystalline structure [20]. The present work gives additional experimental evidence about the formation of the solid solution of tungsten atoms into zirconia lattice to produce two zirconia tetragonal phases, and their further transformation into monoclinic zirconia and orthorhombic WO_3 phases when the sample was annealed at 800 °C.

2. Experimental

2.1. Synthesis

Mixed zirconium tungsten hydroxide was prepared from an aqueous solution of zirconium oxynitrate, $ZrO(NO_3)_2 \cdot 6H_2O$ (Aldrich 99%), and ammonium metatungstate hydrate, $(NH_4)_6W_{12}O_{39} \cdot xH_2O$ (Aldrich 99%). Precipitation was carried out at pH 10 with an aqueous solution of ammonium hydroxide 14 vol% of NH_4OH (J.T. Baker, 28 vol%). The ammonium metatungstate solution was placed in a 4 L container, and the pH was adjusted to 10.0 by adding some drops of ammonium hydroxide solution, in order to have $WO_4^{=}$ species in solution [23]. Thereafter, the zirconium oxynitrate solution was added by dropping together with the remaining ammonium hydroxide solution maintaining the pH constant at 10.0. Herein, a white slurry was obtained by precipitating ZrO_2 in presence of $WO_4^{=}$ species, which must be entrapped in the $Zr(OH)_4$ precipitate.

The obtained white slurry was aged for 24 h at room temperature; then, it was filtered and dried at 110 °C in a vacuum for 18 h (fresh sample). Thereafter, the fresh sample was annealed at 560 °C or 800 °C for 4 h in flowing air.

2.2. Characterization

Elemental analysis was determined on the sample annealed at 800 °C by atomic absorption spectroscopy (AAS) with a Perkin–Elmer 5000 spectrophotometer.

Differential thermal analysis (DTA) was developed on Perkin–Elmer ATD 1700 apparatus from room temperature to 1000 °C. Weight loss curves were determined by Thermogravimetry (TGA) with a Perkin–Elmer TG-7 in the as synthesized sample. The heating rate was 5 °C/min, from room temperature to 1000 °C, flowing air at 20 cm^3/min.

The X-ray diffraction patterns of the samples packed in a glass holder were recorded at room temperature with CuKα radiation in a Bruker Advance D-8 diffractometer having θ–θ configuration and a graphite secondary-beam monochromator. Diffraction intensity was measured in the 2θ range between 15° and 110°, with a 2θ step of 0.02° for 8 s per point.

The Raman spectra were recorded at room temperature using an Yvon Jobin Horiba (T64000) spectrometer, equipped with a confocal microscope (Olympus, BX41) with a laser 514.5 nm emission line at a power of 15 mW. The spectrometer is equipped with a CCD detector.