Influence of Synthesis Methods on Tungsten Dispersion, Structural Deformation, and Surface Acidity in Binary WO₃-ZrO₂ System

M. A. Cortés-Jácome,* J. A. Toledo, and C. Angeles-Chavez

Instituto Mexicano del Petróleo. Prog. Ingeniería Molecular, Eje Central L. Cárdenas # 152, 07730 México D. F., México

M. Aguilar

Universidad Nacional Autónoma de México. Instituto de Física, AP 20-364, 01000 Mexico D. F., Mexico

J. A. Wang

Laboratorio de Catálisis y Materiales, SEPI-ESIQIE, Instituto Politécnico Nacional, Col. Zacatenco, 07738 Mexico D. F., Mexico

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 WO_3 -ZrO₂ catalysts were synthesized by precipitating the aqueous solutions of zirconium oxynitrate and ammonium metatungstate with ammonium hydroxide. The white slurry precipitate was treated under three different conditions. In the as-made materials, the amorphous phase was formed in the aged and refluxed samples, while well-crystallized tetragonal and monoclinic phases were obtained in the hydrothermally treated sample. The real amount of tungsten loaded in the samples was similar for the three samples, independently of the treatments; however, the tungsten surface atomic density in the annealed WO_3 -ZrO₂ samples varied between 6 and 9 W atoms/nm². Two different contrast types of aggregates were determined by scanning electron microscopy, the white particles which are rich in W, and the gray ones which are rich in zirconium; both of them were formed in the calcined solids prepared under aging or reflux condition. A very high dispersion of tungsten species on the zirconia surface was achieved in the hydrothermally treated sample. The degree of the interaction between WO_x and ZrO₂ surface strongly modified the Zr-O bond lengths and bond angles in the structure of tetragonal zirconia as proved by X-ray diffraction analysis and the Rietveld refinement. The catalyst obtained under hydrothermal condition exhibited the highest dispersion of tungsten species in the zirconia, which in turn causes strong structural deformation of the tetragonal ZrO₂ phase responsible of the strongest surface acidity and, consequently, the optimum catalytic activity for *n*-hexane isomerization.

1. Introduction

Solid acid catalysts play an important role in hydrocarbon conversion reactions in the chemical and petroleum industries.^{1,2} In such cases, zirconia is frequently used as catalyst or support. It is well known that zirconia has three stable crystalline phases: tetragonal, monoclinic, and cubic zirconia, and their concentration and transformation between each other depend on zirconia doping and/or thermal treatment. The zirconia doped by a variety of compounds such as sulfate,³ phosphate, and heteropolyacids⁴ creates additional electron-deficient regions that may generate new acid sites and increase the strength of Brönsted acidity responsible for an enhanced catalytic activity in alkanes isomerization reactions.¹⁻⁶ In addition, modifying by these anions mentioned above, tetragonal zirconia phase can be stabilized at high temperature, 6^{-12} which is reported to be favorable in catalytic reactions such as alkanes isomerization. The acidic nature and crystalline structure of zirconia can be also modified by other oxides such as tungsten oxide.9-13 Hino and Arata reported that WO3-ZrO2 mixing oxide is an alternative material in the acid-catalyzing reactions requiring strong acidity.^{5,14} Although the crystalline structure of zirconia has been extensively studied, less attention has been paid on the defective characteristics and distorted crystalline structure of the WO_x species doped zirconia nanophases, which are usually acted as catalytic active sites involving in many catalysis reactions.^{15,16}

The crystalline structures, acidity, and catalytic properties of zirconia-tungsten oxides are greatly dependent on synthesis method. Many synthetic techniques, such as conventional precipitation with different impregnation techniques (evaporation, incipient wetness), microemulsion, and sol-gel, have been employed for the preparation of WO_x -ZrO₂ oxides.^{10,12,17} The thermal treatments suggested are reflux,12 aging,17 and hydrothermal treatment under different temperatures.9 When a precipitation or sol-gel method is used for activation of the solids, a higher annealing temperature than that used for impregnated sample is usually required.^{10,18} This is because solgel solids usually consist of homogeneous phase composition; high temperature favors the formation of active WO₃ phases expelled from the bulk of ZrO₂ on the zirconia surface to form active species responsible for the catalytic activity. It is reported that the WO_x domain depends only on the WO_x surface density and not on the WO₃ concentration in the material.^{1,19} The high activity appears to require the presence of WO_x domains on ZrO_2 surfaces in the binary WO_x - ZrO_2 oxides, however, is

^{*} To whom correspondence may be addressed. E-mail: macortes@imp.mx. Phone: $52\ 55\ 91\ 75\ 84\ 33.$ Fax: $+\ 52\ 55\ 91\ 75\ 62\ 39.$

 TABLE 1: Atomic Fractional Coordinates of Tetragonal Zirconia (P42/ nmc)

atom	site	Х	У	Z
Zr	2a	0.75	0.25	0.75
O	4d	0.25	0.25	u ^a

^{*a*} *u* varied between 0.441(1) and 0.452(2).

usually affected by thermal treatment conditions. Comparative studies of the influences of the synthetic conditions on the active structure, surface acidity and catalytic property of the binary WO_x -ZrO₂ oxides are quite interesting.

In the present work, syntheses of a series of WO_x-ZrO_2 prepared by use of the precipitation technique are reported. The resultant materials were treated through three different routes: aging, refluxing, and hydrothermal conditions at a desired temperature. The crystalline structure of the materials were characterized with the X-ray diffraction (XRD) technique and carefully refined by the Rietveld method; the surface nature and morphological features were studied by using back-scattered scanning electron microscopy (SEM) and Fourier transform infrared (FT-IR) spectroscopic methods, and the textural properties, including surface areas and pore size distribution, were determined by the Brunauer–Emmett–Teller (BET) method. Finally, the catalytic activity and selectivity of the WO_x-ZrO_2 catalysts for *n*-hexane isomerization reaction are reported.

2. Experimental

2.1. Synthesis of Materials. A mixed zirconium tungsten hydroxide was prepared from aqueous solution of zirconium oxynitrate, ZrO(NO₃)₂·6H₂O (99%) 0.2 M, and ammonium metatungstate hydrate, $[(NH_4)_6W_{12}O_{39}.xH_2O, 99\% + 80 \text{ mesh}]$ 0.007 M. The precipitation was carried out at a pH between 9.5 and 10 with an aqueous solution of ammonium hydroxide 14 vol % of NH₄OH (28 vol %) as a precipitating agent. The ammonium metatungstate solution was placed into a 4-L container, and the other two solutions were added slowly to the former one. A constant and vigorous agitation was maintained during the precipitation procedure. The obtained white slurry was split into three parts; one of them was aged for 24 h at room temperature (hereinafter referred to as WZA), another part was refluxed at 373 K for 24 h (hereinafter referred to as WZR), and the last part was hydrothermally treated in a stainless steel autoclave at 468 K, with autogenous pressure (hereinafter referred to as WZH). All samples were dried at 383 K for 18 h; before characterization, dried powders were annealed at 1073 K for 4 h in anhydrous air flow.

2.2. Characterization. The atomic tungsten concentration in the annealed materials was determined by atomic absorption spectroscopy with a Perkin-Elmer 5000 spectrophotometer.

XRD patterns of the samples packed in a glass holder were recorded at room temperature with Cu Kα radiation in a Bruker Advance D-8 diffractometer having $\theta - \theta$ 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. Crystalline structures were refined with the Rietveld technique using DBWS-9411²⁰ and FULLPROF-V3.5d codes;²¹ peak profiles modeled with a pseudo-Voigt function contained average crystallite size as one of its characteristic parameters.^{22,23} To refine the crystalline structures of the solids by the Rietveld method, the tetragonal unit cell symmetry was described with the $P4_2/nmc$ space group, with atomic positions given in Table 1. Monoclinic unit cell symmetry was modeled with a unit cell that had symmetry of $P2_1/c$ space group and the positions of the atoms are given in

 TABLE 2: Limits of the Atomic Fractional Coordinates of Monoclinic Zirconia $(P2_1/c)^a$

atom	site	Х	У	Z
Zr	4e	0.259(1)-0.269(2)	0.031(1)-0.038(1)	0.208(1)-0.213(1)
0(1)	4e	0.065(7) - 0.134(7)	0.326(6)-0.367(4)	0.345(5)-0.365(3)
O(2)	4e	0.468(7) - 0.492(4)	0.748(2) - 0.774(4)	0.437(5)-0.464(6)

 $^{\it a}$ The first value is the lower limit, and the last value is the upper limit.

Table 2 and have been reported elsewhere.²⁴ The WO₃ structure was modeled with an orthorhombic unit cell that had the symmetry of *Pmnb* space group.²⁵ Standard deviations, which show the variation of the last digit, are given in parentheses and have been reported elsewhere.²⁶

BET surface areas, pore volumes, and pore size distribution were obtained by nitrogen physisorption in an ASAP-2000 analyzer from Micromeritics.

Samples were characterized by FT-IR spectroscopy using a 170 SX Nicolet spectrometer. Self-supported wafers (\sim 14 mg) were mounted in a glass cell equipped with KBr windows, which allowed following spectrum variations with thermal treatments. The sample was outgassed at 273 K under 60 mL/min dried airflow for 1 h before the IR spectrum measurement. For the acidity measurements, the sample was treated in an IR cell under vacuum conditions (10^{-4} Torr) at 673 K for 2 h and then cooled to room temperature; the IR spectra of the calcined solid were recorded too. Pyridine was adsorbed on the wafer at room temperature, evacuated and heated at various temperatures.

The samples were analyzed in an environmental scanning electron microscope XL30, which was attached to an X-ray energy dispersive spectroscope (EDAX). The SEM micrographs were taken with backscattering electrons in order to obtain compositional images.

2.3. Catalytic Evaluations. The catalytic activity was measured in *n*-hexane isomerization reaction, and it was carried out at 2 kg/cm² pressure and 533 K in a continuous flow fixedbed microrreactor. Powdered solids (0.1 g) were loaded into the reactor, and 0.2 mL/min of *n*-hexane and 3.12 mL/min of hydrogen were fed. *n*-hexane molar flow was 3.19×10^{-5} mol/h, and the H₂/*n*-hexane ratio was 8.19. Thus, the weight hourly space velocity (WHSV) was 1.92 h^{-1} . The product gas mixture was analyzed online with a Varian 3400 gas chromatograph equipped with a flame ionization detector (FID) and a 50-m methyl silicon gum capillary column. The conversion was kept below 10 mol % at 5 min of time on stream. Before each reaction test, the catalysts were activated in situ at 623 K in 80 mL/min dry N₂ flow for 2 h, cooled at 533 K under flowing N₂, then *n*-hexane reactant was admitted to start the reaction.

3. Results

3.1. XRD Analysis. The XRD patterns of as-synthesized WZA and WZH samples, obtained under different conditions, are shown in Figure 1. Only an amorphous phase corresponding to the hydroxylated zirconia was observed in the sample obtained by aging precipitation at room temperature (WZA) and refluxed at 373 K (WZR) (not shown). Well-crystallized tetragonal and monoclinic zirconia phases were obtained when the precipitate was treated under hydrothermal conditions (WZH), Figure 1. When these as-made materials were calcined at 1073 K in an air flow, both tetragonal and monoclinic zirconia phases were formed (Figure 2). The presence of WO₃ orthorhombic phase was evident only in WZR and WZA samples, whereas the material prepared by hydrothermal treatment, WZH,



Figure 1. XRD patterns of WZC and WZH as-synthesized samples dried at 373 K. Upper tick marks correspond to the tetragonal zirconia phase and the lower ones to the monoclinic zirconia phase. Miller indices are indicated with "t" for tetragonal and with "m" for monoclinic phases.



Figure 2. XRD patterns of WO₃-ZrO₂ samples annealed at 1073 K. Upper tick marks correspond to the tetragonal zirconia phase, their corresponding Miller indices are marked with a "t", and the middle tick marks correspond to the monoclinic zirconia phase, their corresponding Miller indices are marked with "m". The lower ones correspond to orthorhombic WO3 phase, their Miller indices are indicated with "w" in the amplified inset from $2\theta = 22-26$.

did not show any characteristic XRD peaks corresponding to orthorhombic WO₃ phase.

The crystalline phases in the calcined materials were refined by using the Rietveld method. Figure 3 shows a typical plot of the Rietveld refinement corresponding to WZR sample. The results of the Rietveld refinements (see Table 3) confirmed that the concentration of tetragonal zirconia phase in the tungsten containing samples is higher than 60 wt. %. Whereas, pure ZrO₂ solid, annealed at 973 K, consisted of only 30 wt. % of tetragonal phase. This result suggests that the presence of tungsten stabilizes the metastable tetragonal phase at 1073 K and inhibits the phase transformation to monoclinic crystals.^{6–12} On the other hand, formation of the tetragonal phase also depends on the aging treatments of the precipitate: higher concentration of this phase can be retained when the precipitate was crystallized under hydrothermal condition (74 wt %).

The crystallite size of the tetragonal zirconia in the three samples varied with preparation conditions, it was 23 nm in

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Figure 3. Rietveld refinement plot of the sample WZR annealed at 1073 K ($R_{wp} = 0.147$). Crosses correspond to the experimental data and the continuous line to the calculated ones. The difference between experimental and calculated data is also shown with a continuous line. Upper tick marks correspond to tetragonal zirconia phase ($R_{\rm B} = 0.017$), middle tick marks to monoclinic zirconia phase ($R_{\rm B} = 0.039$), and the lower ones to the orthorhombic WO₃ phase ($R_{\rm B} = 0.066$).

TABLE 3: Crystallite Size and Phases Compositions **Determined by Rietveld Method**

	annealing temperature	crystallite size (nm)			phase composition (wt. %)		
sample	(K)	t-ZrO ₂	m-ZrO ₂	WO _x	t-ZrO ₂	m - ZrO_2	WO _x
ZrO ₂ WZA WZR WZH	973 1073 1073 1073	12.0(3) 23.2(4) 15.7(2) 16.6(2)	18.3(4) 18(1) 16.1(5) 19(1)	5.3(4) 48 (6)	30.46 63.4(4) 59(2) 74.28	69.54 25(2) 33.65 25.72	11.3(5) 7.16

TABLE 4: Lattice Parameters of Tetragonal Zirconia

sample	<i>T</i> (K)	a = b (nm)	<i>c</i> (nm)
ZrO_2	973	0.35979(6)	0.5177(1)
WZA	1073	0.35953(3)	0.51885(5)
WZR	1073	0.3594(2)	0.51823(5)
WZH	1073	0.35928(3)	0.52013(6)

WZA, 15.7 nm in WZR, and 16.6 nm in WZH solid. However, the crystallite size of monoclinic zirconia was approximately 18 nm, independent of the aging treatment.

The lattice parameters of tetragonal zirconia are reported in Table 4. It was noted that the structure of tetragonal zirconia was distorted in comparison with that in the pure zirconia solid; it is expanded in the c axis but contracted in a direction, when tungsten was incorporated into the zirconia structure.

3.2. SEM Images and Energy-Dispersive Spectrometry (EDS) Analysis. To observe the surface morphologies and tungsten distributed on the surface of zirconia solids, the three samples, annealed at 1073 K, were analyzed by SEM using backscattering electron images. Figure 4 shows compositional images and chemical analysis of white and gray contrasts presented in each sample. Small white particles on the surface of the big gray particles were usually observed in WZA and WZR samples (see parts a and b of Figure 4). However, small gray particles with a similar size as the white particles are also presented in the surface of the big particles. The sizes of the gray particles in WZA are bigger than those in WZR sample; however, the white particles in the WZA sample are smaller than those presented in the WZR sample. In the case of the WZH sample (see Figure 4c), it is constituted mainly by big and small particles with only one kind of contrast. Similarly, the smaller particles are also deposited on the surface of the bigger particles in this solid.

The SEM images suggest that the gray particles are mainly constituted by zirconia, while the white particles are rich in W. This is because the image formation process is based on the



Figure 4. Backscattering SEM micrographs of the samples (a) WZA, (b) WZR, and (c) WZH annealed at 1073 K and EDS spectra corresponding to (d) white particles, (e) big gray particles, and (f) small gray particles.

backscatter electrons of the atoms present in the sample: W atoms scatter more electrons than Zr atoms, due to W greater atomic number compared to that of Zr. This condition must produce white contrast images where high W concentration is present.

Typical EDS spectra, recorded from the white particles in the sample WZA (see Figure 4d), showed a higher W peak intensity than those observed for O and Zr atoms. The chemical composition determined by this analysis showed that the white particles are basically composed of 61.05 wt. % W atoms, 22.27 wt. % Zr atoms, and 16.68 wt. % O atoms. The EDS obtained from gray agglomerates (see Figure 4e), showed that the largest peak corresponds to Zr atoms, which means that these gray particles are composed mainly of Zr atoms (14.48 wt. % of W atoms, 62.36 wt. % of Zr atoms, and 23.16 wt. % of O atoms). Chemical composition of the more homogeneous gray agglomerates in WZH sample (see Figure 4f), showed a similar concentration of O and Zr atoms, but the W atoms concentration was slightly higher, 19.00 wt. %, than that observed in the gray contrast agglomerates from Figure 4b for WZR sample, suggesting a more homogeneous dispersion of WO_x on the zirconia surface.

To obtain stronger evidence about WO_x dispersion on the surface of zirconia, chemical mapping of the compositional images was carried out at higher magnification. Figure 5 shows the chemical distribution of O, W, and Zr atoms on the surface of particles in WZR sample. Oxygen atoms are distributed uniformly on the surface of the particles. The W atoms showed high concentration in the areas where white particles are deposited, whereas mapping of Zr atoms were deficient in those regions; this can be appreciated as holes in the corresponding chemical Zr map. From this analysis, it can be concluded that the small gray particles have the same chemical concentration as the big ones on which they are deposited, because it did not show an appreciable variation on the chemical distribution on the surface analyzed. Similar results were obtained in the WZA sample (not shown). The chemical elemental maps of WZH sample are shown in Figure 6. Although this sample showed



Figure 5. Chemical mapping of oxygen, zirconium, and tungsten atoms in WZR sample annealed at 1073 K.



Figure 6. Chemical mapping of oxygen, zirconium, and tungsten atoms in WZH sample annealed at 1073 K.

particles with only gray contrast type in backscatter image, it exhibited inhomogeneous distribution of tungsten and oxygen atoms on the surface of the agglomerates. The concentration of W and O atoms slightly increased in some areas, suggesting that there are some regions on the particles having high concentration of WO_x species, even though they remain in low crystallite size, that is, less than 3 nm. The chemical composition between the particles of different contrasts observed in compositional images was investigated by line scan images. Their composition profiles are shown in Figure 7. The W composition profile of WZA sample (see Figure 7a) shows a low W concentration in the big gray particle surface but a high W concentration in the white particles. In contrast, the Zr composition profile showed a decrease in the



Figure 7. Chemical composition profile of oxygen, zirconium, and tungsten atoms along the line drawn in the corresponding micrographs of the samples (a) WZA, (b) WZR, and (c) WZH annealed at 1073 K.

corresponding regions where the particles are rich in W atoms. The oxygen composition profile exhibited a slight increase in the regions where the white particles are deposited. The WZR sample presented a low O atom concentration profile in comparison with that of Zr and W atoms (Figure 7b), and it did not vary along the white and gray particles. Variations of the profiles of W and Zr atoms in WZH are shown in Figure 7c, Zr atoms concentration is rich in the gray regions, while W atoms is slightly rich in the small gray particles. These results confirm that the gray particles are related to ZrO₂ phase and that the white particles are related to WO_r species. For the hydrothermally treated sample, i.e., WZH, the O atom concentration profile showed a similar behavior as that in Figure 7a; its concentration increased in the regions where W atoms concentration increased. It is interesting to note that this behavior in the O atoms concentration was not observed in WZR sample, where the WO₃ crystallite size was very large. Therefore, it appears that the increase in oxygen concentrations in the regions enriched with W atoms is dependent on the crystallite dimensions of WO_x species.

TABLE 5: Textural properties of the samples calcined at1073 K.

surface area $(m^2 g^{-1})$	porous volume (cm ³ g ⁻¹)	mean porous size (Å)
48	0.073	61
66	0.694	226
54	0.164	77
	$\frac{\text{surface area}}{(\text{m}^2 \text{ g}^{-1})}$ $\frac{48}{66}$ 54	$\begin{array}{c c} surface area \\ (m^2 \ g^{-1}) \end{array} \begin{array}{c} porous \ volume \\ (cm^3 \ g^{-1}) \end{array} \\ \hline 48 & 0.073 \\ 66 & 0.694 \\ 54 & 0.164 \end{array}$

3.3. Textural Properties. The interaction between WO_x species and ZrO_2 in the solids prepared with different aging conditions not only stabilizes the tetragonal zirconia phase and produces a significantly deformed structure but also affects the specific surface area and pore size distribution. The specific surface areas were not quite different between the samples, which varied from 48 to 66 m²/g for ZWA and ZWR samples, respectively, as shown in Table 5. When examining the hysteresis loop shape of the nitrogen adsorption–desorption isotherms in Figure 8, information about pore blocking and pore structure can be obtained. The isotherms presented by the three materials correspond to type IV in the Brunauer, Deming, Deming, and Teller (BDDT) classification.²⁷ The initial sloping



Figure 8. The hysteresis loops of the nitrogen adsorption-desorption isotherms of the different samples calcined at 1073 K.



Figure 9. Pore diameter distributions of the different samples calcined at 1073 K.

characteristic of the descending boundary curves reflects porous structure shrinkage caused by the stress change of the condensate during depressurization, and the sharp decline in the desorption curve at relative pressure of 0.4, 0.6, and 0.7 for the WZA, WZR, and WZH, respectively, indicates the mesoporous characteristics of the material, with different pore diameters (see Table 5 and Figure 9). This type of hysteresis loop has been attributed to either ordered or disordered packed tubes in M41S mesostructures or to wormholelike morphologies shown by very small crystallite size material.^{28–30} In the WZR sample, an additional hysteresis loop can be observed at between 0.9 and 1.0 relative pressure, with relatively high adsorbed volume, which is presumably attributed to the surface of large crystallites of WO₃ phase deposited on the zirconia phases, in agreement with our SEM and XRD results.

The pore volume and pore diameter of the WZA solid is lower than those for WZR and WZH samples. The samples aged at high temperature, that is, WZR and WZH, developed very narrow and homogeneous pore size distributions (see Figure 9), while WZA aged at room temperature showed a broad pore size distribution with relatively low pore volume. Therefore, aging the precipitate by reflux or crystallizing under hydrothermal condition is necessary to develop high porosity in the resulting materials.

3.4. Atomic Absorption Spectroscopy (AAS) Analysis. Chemical composition of the samples determined by AAS showed that the lowest tungsten content (11.6 wt %) was obtained in the room temperature aged sample, WZA, as shown in Table 6; and the high W content (about 15 wt %) appeared in the refluxed and hydrothermal aging samples. By consideration that the calculated W amount was 15% loaded in all the

TABLE 6: Tungsten Concentration and Density on theZirconia Surface of the Samples Calcined at 1073 K

sample	W (wt. %)	W (atoms/nm ²) ^a	W (atoms/nm ²) ^b
WZA WZR	11.6 15	7.92 6.55	2.32 4.45
WZH	14.5	8.79	8.79

^{*a*} Determined taking into account the total amount of W atoms loaded determined by AAS. ^{*b*} Determined by subtracting the amount of W atoms segregated as WO₃ (determined by Rietveld analysis) to the total amount of W atoms determined by AAS.



Figure 10. FTIR spectra of the different samples calcined at 1073 K.

samples and that, at pH = 10.0, tungsten is present mainly as $WO_4^{=}$ species in solution,¹³ one can conclude that when aging the precipitate at room temperature only 64% of the total WO₄ oxoanions interact with the zirconium hydroxide precipitate; however, when the samples were thermally refluxed or crystallized under hydrothermal conditions, almost all WO₄ oxoanions were retained by the zirconium hydroxide or by the crystallized zirconium oxide. Then, thermal treatment aging at 373 K is required to obtain a solid in which tungsten ions completely incorporate into the crystallites of zirconium precipitate.

The density of surface atomic tungsten was determined by taking into account the specific surface area (see Table 5), and the amount of tungsten loaded was determined by atomic absorption (see Table 6, column 3), assuming that all tungsten atoms loaded on zirconia are homogeneously distributed. However, this assumption is not valid for WZR and WZA, where the WO₃ phase was segregated forming aggregates on the surface of zirconia. Then, to estimate this value, the amount of W atoms that in fact plays the role of stabilizing the zirconia phases was estimated by the difference between the total amounts of W atoms (determined by AAS) minus the amount of W atoms segregated as WO₃ (determined by Rietveld analysis), this value is reported in the last column of the Table 6.

3.5. FTIR Analysis. Figure 10 shows the different FTIR spectra of the samples calcined at 673 K in the range of 1500–400 cm⁻¹. Regardless of the preparation methods, all the samples showed a band at 970 cm⁻¹, which was assigned to polytungstate structure with tungsten in octahedral coordination.³¹ Therefore, symmetrical W=O stretching vibration was assigned to octahedrally coordinated WO_x species on the surface of tetragonal ZrO₂. This unique vibration mode was observed on the WZH sample, because the WO_x species were more



Figure 11. In situ FTIR spectra of pyridine adsorption on the samples calcined at 1073 K. The samples were thermally treated in the IR cell at different temperatures: (a) ambient temperature and (b) 573 K.

homogeneously distributed on the surface of zirconia. This band appeared at lower wavenumbers than those reported in other works, which are between 1000 and 1020 cm⁻¹.^{10,32,33} The shift of the band position toward lower wavenumbers (970 cm⁻¹) in our samples could be attributed to a strong tungsten–zirconia interaction,³⁴ which could be in turn explained by the neutralization of the basic sites in ZrO₂ by tungstate anions; this aspect will be later discussed in this paper.

Two additional FTIR bands at 508 and 743 cm⁻¹ were observed in the WZA sample, in which the WO₃ phase was segregated with a 5.23(4) nm crystallite size. These two additional peaks were also observed in the WZR solid, and they could be assigned to the W–O vibration of tungsten species bonded on the surface of ZrO₂, as observed on the samples of 10 wt. % W/ZrO₂ prepared by precipitation or sol–gel, where they were assigned to a W–O vibration of crystalline and noncrystalline tungsten species.¹⁰ However, from this study it can be established that the FTIR bands at 743 and 508 cm⁻¹ appear only when the WO₃ phase presents some crystalline order with crystallite size larger than 5 nm. FTIR analysis of the WZR presented three additional bands at 1400, 1260, and 1100 cm⁻¹, which are assigned to the well crystallized WO₃ phase.⁹

3.6. Surface Acidity. The FTIR spectra of adsorbed pyridine evacuated at 298 K (see Figure 11a) showed Lewis and Brönsted acid sites in all the samples and the intensities of the corresponding vibration bands on the WZH sample were higher than those on the WZR and WZA solids. Hence, the sample prepared by hydrothermal treatment showed high acid density, which is related to its high density of surface atomic tungsten.

When the samples were heated at 573 K under vacuum conditions, the vibration bands of the adsorbed pyridine on Lewis and Brönsted acid sites remained with considerable intensity only in the WZH sample (see Figure 11b). In the refluxed WZR sample, some broad peaks, which could be confused with the background, suggest that a little amount of Brönsted and Lewis acid sites were still retained in this sample, whereas in the WZA sample, practically all the pyridine was desorbed at 573 K. From these results, one can conclude that the acid strength on WO_x -ZrO₂ catalysts obviously depends on the tungsten density, as indicated in Table 6. In other words, the higher atomic tungsten density on the surface, the higher the Brönsted and Lewis acidity.

 TABLE 7: Activity and Selectivity Results of the Samples

 Calcined at 1073 K

	conversion		selectivity (mol %)			
sample	(mol %)	cracking	2,3DMB	2MP	3MP	
ZrO ₂	0	0.0	0	0	0	
WZA	4.23	0.0	15.3	52.62	32.08	
WZR	6.98	0.0	15.4	52.85	31.75	
WZH	8.16	1.94	14.66	51.3	32.09	

3.7. Catalytic Properties. Catalytic activity and selectivity of *n*-hexane isomerization over the three catalysts are reported in Table 7. The highest conversion was observed in the hydrothermally treated WZH sample, which corresponded to the sample with the highest tungsten dispersion or the highest surface atomic tungsten density, consequently the highest density of Brönsted and Lewis acid sites. Small amount of cracking products were identified when WZH was used as catalyst, which could be associated to the strongest surface acidity. The selectivity to the isomers on the other two samples reached 100% without any cracking products. The main products in the *n*-hexane isomerization were 2,3-dimethyl butane (2,3DMB), 2-methyl pentane (2MP), and 3-methyl pentane (3MP) for all the samples. The selectivity to these products was quite similar in all the samples.^{35,36}

4. Discussion

4.1. Effect of Different Treatments on the Phase Formation and Crystallite Size. XRD analysis shows that the materials obtained under different treatment conditions had quite different phase compositions. For instance, in the as-synthesized WZH solid, 74 wt. % of the tetragonal zirconia was already formed, then WO₄⁼ species interacted with the surface of wellcrystallized zirconia phases during the hydrothermal treatment. However, in samples prepared by aging the slurry at room temperature and refluxing at 373 K, the resultant solids are in amorphous state, then WO4⁼ species must interact with the amorphous hydroxylated zirconia phase, where tungstate species stabilize the material in 100 wt % tetragonal phase even after annealing at 973 K, as was reported elsewhere.¹⁶ When the samples were annealed at 1073 K, a certain amount of WO_x crystallites, which are then partially transformed into the orthombic phase, segregates from tetragonal zirconia. These results can be explained by assuming that, during precipitation and aging treatment (but not under hydrothermal crystallization condition), WO₄⁼ species are trapped inside the zirconia hydroxide polymeric species [Zr₈(OH)₂₀(H₂O)₂₄]¹²⁺, followed by transformation of the octamer to larger aggregates, forming bidimensional sheets or three-dimensional agglomerates with rapid nucleation.³⁷ Finally, a solid $W_x Zr_{1-x}O_2$ solution was formed by isomorphic cationic substitution of zirconium atoms by tungsten atoms in the lattice of the tetragonal zirconia, when annealing at 973 K.¹⁶ After annealing at 1073 K, the tetragonal structure partially collapses segregating WO₃ crystallites.

The tungsten incorporation also affects the crystallite size of the tetragonal zirconia phase (see Table 3). In pure ZrO_2 sample, low concentration of tetragonal zirconia was present; however, its crystallite size was (12 nm) smaller than that of the tungsten containing samples (16–23 nm). The largest crystallite size of tetragonal zirconia was formed in the ZWA sample annealed at 1073 K. In all cases, with and without tungsten, the tetragonal zirconia phase has been stabilized at crystallite sizes between 12 and 23 nm, which is lower than that obtained under nonhydrostatic stress as reported by Garvie.³⁸

The crystallite size of the orthorhombic phase of WO₃ loaded on the different solids was quite different, strongly depending



Figure 12. Representative polyhedron of the tetragonal crystalline structure of zirconia.

 TABLE 8: Atomic Bond Lengths and Bond Angles of Tetragonal Zirconia

$T(^{\circ}C)$	T (K)	d_1 (nm)	d_2 (nm)	ϕ	δ
ZrO_2	973	0.21242(6)	0.23162(6)	115.74(2)	113.38(2)
WZA	1073	0.20806(6)	0.23715(6)	119.53(2)	115.18(2)
WZR	1073	0.20799(6)	0.23691(6)	119.53(2)	115.13(2)
WZH	1073	0.20536(6)	0.24094(6)	122.04(2)	116.37(2)

on the aging treatment. Large crystallite size (48 nm) was obtained in the WZR sample. However, in the WZA sample its crystallite size was 5.3 nm. In the WZH sample, there were not any WO₃ crystals detected by XRD analysis, indicating that WO_x species are highly dispersed on the surface of zirconia with a crystallite size less than 3 nm. It is very likely that in this sample WO_x species are strongly bounded to the surface of the zirconia. Therefore, the various aging treatments on the zirconia precipitate result in different degrees of interaction between WO_x species and zirconia surface, leading to WO₃ crystallites with different dimensions.

4.2. Effect of Different Treatments on the Crystalline Structural Deformation. Noteworthy, the unit cell of tetragonal zirconia in the tungsten-containing solids, relative to the pure zirconia structure, was expanded only along the c direction, while along the other directions, a and b, it remained almost constant. This fact must be indicative of strong variations in the tetragonal local order structure. In pure ZrO₂, the tetragonal lattice parameter c was 0.5171(1) nm. The refluxed WZR sample, where larger WO₃ crystallite size was formed, suggests a weak interaction between tetragonal ZrO_2 and WO_x species, showing a lattice c parameter of 0.51823(5) nm, only slightly larger than that in pure tetragonal ZrO₂. However, the WZH sample, where the WO_x species were well dispersed on the tetragonal ZrO₂ phase with crystallite size less than 3 nm, showed a lattice c parameter of 0.52013 (6) nm, an increment of 3% was obtained. In this sample, strong interaction between WO_x and tetragonal ZrO_2 must exist. Hence, the changes in lattice c parameters in the structure of tetragonal zirconia may be indicative of the interaction degree between WO_x and tetragonal ZrO₂.

In the unit cell of tetragonal zirconia, there are two different Zr–O bonds with different length, referred to as d_1 and d_2 (see Figure 12), with two different O–Zr–O bond angles, ϕ , the angle formed between two d_1 bond lengths, and δ , the angle formed between two d_2 bond lengths.¹⁶ All the data related to Zr–O bond lengths and bond angles are reported in Table 8. It is interesting to examine how Zr–O bond lengths and bond angles change as a function of the interaction degree between tetragonal ZrO₂ and WO_x species. Rietveld refinements showed that the Zr–O (d_1) bond length was 0.21242(6) nm for pure tetragonal ZrO₂, and it decreased to 0.20536(6) nm in the WZH sample, calcined at 1073 K, where WO_x species were well dispersed. In the aged and refluxed samples (WZR and WZA), the d_1 bond lengths remain quite similar (0.20806(6) and 0.20799(6) nm, respectively). In these two samples, WO₃



Figure 13. Lattice of the tetragonal zirconia phase projected perpendicular to the c axis.

segregated from tetragonal zirconia, decreasing the interaction between tetragonal ZrO_2 and WO_3 phase, thus, as a result, their d_1 bond lengths remained between the values of pure tetragonal ZrO_2 and WZH solids. The Zr–O bond lengths, d_2 , increased from 0.23162(6) nm for pure tetragonal ZrO₂ to 0.24094(6) nm for WZH. On the other hand, WZR and WZA samples showed a Zr–O bond length (d_2) quite similar, that is, 0.23715(6) and 0.23691(6) nm, respectively. All these data clearly show that the crystalline structure of tetragonal zirconia was strongly deformed after tungsten incorporation, depending on the degree of the interaction between tetragonal ZrO₂ and WO₃ phases.

The structural deformation of the tetragonal ZrO₂ structure was also reflected in the variations O–Zr–O angles. Both, ϕ and δ angles increased as the interaction degree between WO_x species and tetragonal ZrO₂ increased in WZH sample, remaining constant for WZA and WZR samples, where WO₃ phase was segregated.

All the above results point out structural parameters of the tetragonal zirconia are very sensitive to the interaction degree between WO_x species and the surface of tetragonal ZrO_2 phase. The expansion of the tetragonal structure only along the cdirection and the increase in the $Zr-O(d_2)$ bond lengths suggests that WO_x species are bonded to the oxygen atoms exposed on the surface perpendicular to the c axis (see Figure 13), because all the oxygen atoms exposed at the top layer of the (001) plane are bonded to the zirconium atoms with a d_2 Zr–O bond length. Hence, the increase in the d_2 dimension, Zr–O bond length, as the interaction degree between WO_x species and the surface of tetragonal ZrO₂ increases could be related to the electron effect of the WO_x species (attractor or acceptor). The strong interaction between WO_x species and the surface of tetragonal ZrO2 leads to electronic deficiency around the Zr^{4+} nuclei, thus, the d_1 bond length must decrease in order to compensate such an electronic deficiency around the Zr⁴⁺ nuclei caused by the elongation of the d_2 bond.

4.3. Effect of Different Treatments on the Surface Acidity and Catalytic Activity. It has been established that segregation of large crystallites of WO₃ on the zirconia surface improves the acidity and catalytic properties of the WO_x-ZrO₂ catalysts;^{12,18} however, large amount of the tungsten species are not exposed to the surface in well-crystallized WO₃, therefore, a question can be formulated: are well-crystallized WO₃ phase or dispersed WO_x species that stabilize the tetragonal ZrO₂ phase responsible for the high acidity? This question can be answered by analyzing the acidity and catalytic property of the three samples treated in a variety of conditions. Figure 11 shows that the WZH solid had not only the largest number of both Brönsted and Lewis acid sites but also the strongest acidity. Because the dispersion of WO_x species in the WZH solid was very high and uniform, it is reasonable to conclude that highly dispersed WO_x species are mainly responsible for the generation of acidity. As discussed above, the crystalline structure of the zirconia phase in WZH sample shows the strongest deformation that resulted from the strongest interaction between the WO_x species and zirconia, due to the highest dispersion of WO_x species, therefore, the deformation of the crystalline structure is also correlated well with acidity of the solid.

The catalytic activity showed the same trend as that observed in the population of Brönsted and Lewis acid sites. The relatively highest conversion of *n*-hexane was achieved on the sample with the highest surface tungsten density. WO_x species homogeneously distributed on the surface of the tetragonal ZrO_2 are the active species that participate in the reaction, and that well crystallized WO_3 phase with large particles size are less active for the *n*-hexane isomerization reaction.

5. Conclusions

Binary WO₃–ZrO₂ solids with different phase compositions and structural distortion were synthesized by use of the coprecipitation method under a variety of aging conditions. The solids aged at room temperature or refluxed at 373 K for 24 h showed an amorphous phase, which may segregate nanocrystals of WO₃ with a size larger than 5 nm from the phase of tetragonal zirconia after 1073 K of calcination. However, when the sample was hydrothermally treated in an autoclave, well-crystallized phases of tetragonal and monoclinic zirconia were formed in the dried material, and even when it was calcined at 1073 K, not any WO₃ nanocrystals larger than 3 nm were segregated, indicating a very high dispersion of tungsten species. All the materials showed mesoporous textures with surface area between 48 and 66 m²/g and average pore diameter between 5 and 10 nm.

The crystalline structure of tetragonal zirconia in the solid obtained in hydrothermal conditions was strongly deformed, as indicated by clear expansion of the lattice *c* parameter and Zr–O bond lengths (d_2) and variations in bond angles (ϕ and δ) that resulted from the strong interaction between WO_x and ZrO₂. However, the structure of zirconia in the materials obtained by aging the precipitate at room temperature and refluxing at 373 K showed only slight distortion, which resulted from weak interaction between WO_x and ZrO₂ because of segregation of large WO₃ crystals.

The sample prepared under hydrothermal treatment conditions exhibited the highest density of surface acid sites, which was responsible for the best catalytic activity in *n*-hexane isomerization; however, due to its stronger acidity, 1.9% of cracking products were produced during the reaction, this differs from the other two catalysts on which selectivity to 100% isohexanes was achieved but with slightly low conversion.

This work provides new experimental information on how to obtain WO_x —ZrO₂ binary oxides with different WO_x dispersions, surface acidity, and catalytic behaviors by treatment the precipitating materials under controllable conditions. It also illustrates how computer simulation (the Rietveld refinement) combined with experimental techniques contributes to interpret the variations of crystalline structure and catalytic properties of the solids. **Acknowledgment.** The financial support from the IMP-D00237 Project is greatly appreciated. We thank Mrs. Rosa Isela Conde Velazco and Mr. Gabriel Pineda Velázquez for their technical assistance.

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(21) Rodríguez-Carbajal, J. Laboratoire Leon Brillouin, France. Phone: (33) 1 6908 3343. Fax: (33) 1 6908 8261. E-mail: juan@llb.saclay.cea.fr.

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