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# Study by high-throughput experimentation of the effect of the pretreatment and precursors on the catalytic activity of tungstated zirconia catalysts

M.L. Hernandez-Pichardo [a,*], J.A. Montoya de la Fuente [b], P. del Angel [b], A. Vargas [b], C. Reza [a]

[a] Instituto Politécnico Nacional, ESIQIE, Laboratorio de Catálisis y Materiales, Av. IPN S/N Zacatenco, 07738 México, Mexico
[b] Instituto Mexicano del Petróleo, Dirección de Investigación y Posgrado, Eje Central L. Cárdenas 152, 07730 México D.F., Mexico

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ABSTRACT

High-throughput experimentation (HTE) was used for the synthesis, characterization and catalytic evaluation of tungstated zirconia (WZ) materials doped with manganese. A library with three series of $MnO_y$–$WO_x$–$ZrO_2$ catalysts was prepared by different methods (surfactant-assisted coprecipitation and impregnation), using different precursors and pretreatments (washing and/or aging). These materials were characterized by XRD, Raman and MET (HRTEM and EDS). Different nanostructures were observed depending on the synthesis method. Highly dispersed $WO_3$ catalysts calcined at 800 °C were obtained by coprecipitation method, while the impregnation method brings the segregation of both, the monoclinic $WO_3$ and $ZrO_2$ phases. The catalytic activity of the Pt-promoted $MnO_y$–$WO_x$–$ZrO_2$ catalysts (0.3 wt.% Pt) was evaluated in the *n*-hexane hydroisomerization reaction. Although, in the coprecipitated catalysts similar $WO_x$ nanostructures were observed, the catalytic activity mainly depends on the zirconia precursor, as well as aging and washing pretreatments, following the order: $ZrOCl_2$ (coprecipitation) > $ZrO(NO_3)_2$ (coprecipitation) ≫ $Zr(OH)_4$ (impregnation). The catalysts with highest activity were pretreated by washing and aging.



## 1. Introduction

Light paraffin isomerization for motor fuel production has been widely studied for the production of fuels, since these processes increase its motor fuel value by increasing its octane number. Particularly, the skeletal isomerization of *n*-hexane is important because it allows the production of high number isomers and the production of clean-burning motor fuels by reducing some of the benzene precursors. This reaction has been investigated on different solid acids such as sulfated zirconia (SZ) [1], tungstated zirconia (WZ) [2], tungstated ceria ($WO_x$–$CeO_2$) [3], as well as different kind of zeolites (Beta, Mordenite, USY) [4], and recently in some more complex materials such as Pt–Ni–$WO_x$/$SiO_2$–$Al_2O_3$ catalysts [5]. It was found that the preparation method of the catalysts is very important because it determines some of the important characteristics of the solids such as the dispersion, structure and metal–support interactions. These properties affect the reducibility, the acid sites and the electronic properties of the catalysts [5]. Even with samples of the same catalytic system, important differences arise when comparing samples obtained by different methods and precursors. In SZ-based catalysts for instance, the acidic and catalytic properties of these materials depend on their preparative history from the formation of $Zr(OH)_4$ precursor to the in situ activation of the final catalysts prior to reactions [6]. In the case of WZ the effect of several synthesis methods and activation procedures have been already tested [7,8]. However, no study so far has focused on the role of the promoters (Mn) and the pretreatment conditions of washing and aging, prior to the calcination, and its effects on the nanostructure and catalytic activity of tungstated zirconia solids.

These catalytic systems are very complex and their preparation depends on several parameters that can affect the nature and structure of the $WO_x$ species supported on the $ZrO_2$ surface, and therefore their catalytic performance. Some synthesis parameters, such as filtration, washing, aging and drying, make the preparation procedure especially difficult for a large number of samples. Recently, the interest of using HTE techniques for the synthesis of catalytic materials has increased [9,10], due to the need for studying different variables, on exactly the same conditions of synthesis, characterization and catalytic evaluation.

In this work the HTE techniques were applied with the aim of evaluating the effects of different synthesis parameters on the catalytic activity of Pt/$MnO_y$–$WO_x$–$ZrO_2$ system. The synthesis parameters studied were: zirconia precursor ($ZrOCl_2$, $ZrO(NO_3)_2$, and $Zr(OH)_4$), pretreatments (aging, washing) and promoter content (0 and 1 wt.% Mn); further the catalytic activity was evaluated in the *n*-hexane isomerization reaction.

* Corresponding author.
*E-mail addresses:* mhernandezp@ipn.mx, martha_hp@hotmail.com (M.L. Hernandez-Pichardo).

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## 2. Experimental

### 2.1. Catalysts synthesis

High-throughput experimentation techniques were applied to synthesize a library of 24 $MnO_y$–$WO_x$–$ZrO_2$ catalysts using a Cavro robot (MSP 9500 by Symyx) by surfactant-assisted coprecipitation or impregnation method. The $Zr(OH)_4$ precursors were: $ZrOCl_2{\cdot}xH_2O$ and $ZrO(NO_3)_2{\cdot}xH_2O$ (abbreviated as Cl and N, respectively), and the catalysts synthesized by impregnation were prepared directly from $Zr(OH)_4$ (abbreviated as OH). The precursors for manganese and tungsten were nitrate $Mn(NO_3)_2{\cdot}xH_2O$ and ammonium metatungstate $(NH_4)_6W_{12}O_{39}{\cdot}xH_2O$ respectively. The surfactant used was an aqueous solution (0.4 M) of CTAB (cetyltrimethylammonium bromide) with a surfactant/zirconia molar ratio = 1. All chemicals were supplied by Aldrich and they were used as received.

The automated synthesis protocol used for the coprecipitation method has been described in our previous work [11]. The solutions of manganese nitrate (0.3 M) and ammonium metatungstate (0.05 M) were gradually dispensed to a solution of the zirconia precursor (0.3 M) and stirred at 60 °C for 1 h. Then an aqueous solution of CTAB (0.4 M) was added, and finally $NH_4OH$ was added to reach a pH 11. After precipitation, only some of the pretreatments were performed depending on the sample. The aging pretreatment was accomplished in the mother liquor at 80 °C for 16 h. Then, washing pretreatment was done with distillate water repeatedly to complete the removal of chloride ions, the excess of surfactant, and/or $NH_4NO_3$ elimination. The elimination was monitored by X-ray fluorescence of the residual liquid. Then the precipitate was filtered after the washing. The elimination of the excess surfactant was monitored by a rapid XRD screening (Bruker-Axs D8 Discover) of the dried samples. Finally, the catalysts were dried at 110 °C for 24 h and calcined in static air at 800 °C for 4 h.

For the catalysts synthesized by impregnation the $Zr(OH)_4$ was impregnated with an ammonium metatungstate solution (0.05 M) and the solids were dried at 110 °C for 24 h. The calcination treatment was also performed in static air at 800 °C for 4 h.

These samples were labeled as WZ($\alpha$)Mn($\beta$)–$\gamma$, where, WZ denotes tungstated zirconia, ($\alpha$) is the zirconia precursor used, ($\beta$) is the manganese content in wt.%, and $\gamma$ means the pretreatment used in the library such as: aging (A), washing (W), aging and washing (AW) and no pretreatment (none).

After calcination at 800 °C, and prior to the catalytic evaluation, the catalysts were impregnated with 0.3 wt.% of platinum with an aqueous solution of $H_2PtCl_6{\cdot}6H_2O$ (Aldrich) (0.3 mg Pt/ml). The Pt loading was maintained constant and only the quantity of sample needed for the catalytic evaluation (100 mg) was impregnated with Pt. The impregnation was performed using the Cavro Robot with a proper protocol previously reported [11] with the aim of not wasting the noble metal. Further, the catalysts were dried at 110 °C and finally calcined at 400 °C in situ for 3 h. In analogy with the previous nomenclature, the resulting materials were denoted as Pt/WZ($\alpha$)Mn($\beta$)–$\gamma$, indicating that these materials have been impregnated with platinum. Table 1 shows the complete description of the library, including the composition (precursor and promoter content), synthesis method (coprecipitation or impregnation) and the pretreatment applied.

### 2.2. Catalytic testing

Catalytic activity was measured in the *n*-hexane hydroisomerization reaction over the Pt/$MnO_y$–$WO_x$–$ZrO_2$ catalysts. The evaluation was carried out in a Combinatorial Multi Channel Fixed Bed Reactor (MCFBR) (Symyx, Tech) fully automated, evaluating 48 samples in parallel. A catalyst sample of 100 mg diluted with 200 mg of inert silicon carbide was loaded in each well and fixed into the reactor heads, containing a set of eight micro-reactors of approximately 4 mm of inner diameter and 47 mm length. The six reactor heads are connected independently to six chromatographs (Agilent, 6850 Series) each one equipped with a SPB-1 capillary column (Supelco) with a length of 100 m, and a flame ionization detector (FID) for the analysis of products. The injection of the reactant and products to the GC's was carried out at the reaction pressure. The reliability of the quantitative method was evaluated with an uncertainty of the conversion ±2% measurable through the 48 wells. The pretreatment of the catalysts was carried out in situ prior to the activity test and it consisted in a drying-reduction program, drying the samples at 260 °C for 2 h in helium (200 $cm^3\ min^{-1}$) followed by reduction in a hydrogen flow (200 $cm^3\ min^{-1}$) at 450 °C for 3 h. Hydrogen and *n*-hexane flows were adjusted to give a $H_2/n\text{-}C_6$ = 1.47 M ratio. The reaction was conducted at 260 °C, 0.689 MPa, 3.7 $h^{-1}$ WHSV and using a mixture of 100 $cm^3\ min^{-1}$ $H_2$ and 0.4 $cm^3\ min^{-1}$ of *n*-hexane fed with an HPLC pump.

**Table 1**
Description of the variables used in the experimental design of the catalysts library: precursor salt (nitrate, chloride and hydroxide), synthesis method (coprecipitation and impregnation), content of promoter (wt.% Mn), and pretreatment (aging, washing, both or none).

| Precursor | Synthesis method | Promoter (%) | Pretreatment[a] |
|---|---|---|---|
| $ZrOCl_2{\cdot}8H_2O$ | Coprecipitation | Mn(0) | A,W, AW, none |
| | | Mn(1) | A,W, AW, none |
| $ZrO(NO_3)_2{\cdot}xH_2O$ | Coprecipitation | Mn(0) | A,W, AW, none |
| | | Mn(1) | A,W, AW, none |
| $Zr(OH)_4$ | Impregnation | Mn(0) | A,W, AW, none |
| | | Mn(1) | A,W, AW, none |

[a] A: aging, W: washing, AW: aging and washing.

### 2.3. Catalyst characterization

$MnO_y$–$WO_x$–$ZrO_2$ nanostructured mixed oxides calcined at 800 °C were characterized by diverse techniques. X-ray diffraction patterns were obtained in a Bruker-Axs D8 Discover with GADDS (General Area Detector Diffraction Systems, two-dimensional detector) diffractometer fitted with a Cu tube (40 kV, 40 mA) using HTE approaches for both, measurements, and patterns evaluation. These materials were studied by HRTEM using a TITAN 80–300 microscope with Schottky type field emission gun, operating at 300 kV and integrated with an imaging aberration corrector. HRTEM digital images were obtained using Digital Micrograph Software from GATAN. Raman spectra of the Mn–$WO_x$–$ZrO_2$ catalysts were recorded in the 100–1200 $cm^{-1}$ wave number range using a ThermoNicolet Raman apparatus (Almega model) equipped with a Nd:YVO4DPSS laser source. The excitation line of the laser was 532 nm and the laser power was of 25 mW.

## 3. Results and discussion

### 3.1. Catalysts characterization

The structure of the $MnO_y$–$WO_x$–$ZrO_2$ library prepared from different precursors, pretreatments, and Mn content (0 or 1 wt.%), was characterized by XRD, Raman and HRTEM. The XRD analysis was performed on the dried (110 °C) and calcined (800 °C) libraries. The Mn–$WO_x$–$ZrO_2$ materials were characterized without Pt because of in this study only the quantity of sample needed for the catalytic evaluation (100 mg) was impregnated with Pt with the aim of not wasting this expensive metal. The diffraction pat-