



## High-throughput study of the iron promotional effect over Pt/WO<sub>x</sub>–ZrO<sub>2</sub> catalysts on the skeletal isomerization of *n*-hexane

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### ABSTRACT

Pt supported on tungstated zirconia catalysts (Pt/WZ) doped with different Fe contents were evaluated in the *n*-hexane hydroisomerization reaction. High-throughput experimentation (HTE) approaches were used to investigate the effect of the iron incorporation over the catalytic activity. It was found that the presence of iron at low concentrations (0.5–1 wt%) increases the conversion and the yield to the high octane 2,2-dimethyl-butane (2,2-DMB) isomer. The characterization results suggest that the presence of iron modifies the nanostructure of the WO<sub>x</sub> species on the zirconia surface which in turn produces the generation of active Brønsted acid sites thus optimizing the tungsten content toward the highest catalytic activity. It was also found that the surfactant incorporation further improves the performance of Pt/WZ catalysts, although, the activity was improved with the Fe addition at lower concentration.

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### 1. Introduction

The hydrocarbons hydroisomerization process is widely employed in the production of both fuels and petrochemicals. Particularly, the *n*-hexane hydroisomerization allows an increase in total gasoline pool octane free of aromatics and benzene precursors due to the production of isomers with high octane number. Solid acids such as sulfated zirconia (SZ) and tungstated zirconia (WZ) catalysts have attracted wide interest due to their high activity and selectivity for *n*-alkanes isomerization processes [1–3]. In addition, the use of some promoters has shown to improve the activity of these catalytic systems; iron- and manganese-promoted sulfated zirconia for example, catalyzes isomerization reactions two or three orders of magnitude faster than sulfated zirconia [4]. On the other hand, it has been found that although Fe and Mn promote sulfated zirconia for *n*-pentane isomerization, they do not promote tungstated zirconia at the same time [5]. However the individual role of iron or manganese is still not clearly understood.

In a study of individual promoters, Jatia et al. [6] found that the incorporation of either Fe or Mn to sulfated zirconia increases the catalytic activity but the Mn impregnated sample shows lower

activity than the Fe impregnated catalysts. Some other works have been dedicated to the study of the different modifiers for nanocrystal zirconia on W/ZrO<sub>2</sub> catalysts [7], and recently our group published some works about the influence of the addition of Mn in Pt/WZ catalysts; we found through high-throughput experimentation approaches that Mn modifies the interaction of the WO<sub>x</sub> species with the support but the catalytic behavior is not a linear function of the Mn composition [8].

In the particular case of iron as a promoter of WZ catalysts, several works have been reported [9–13]. Santiesteban et al. [9] found that the Fe incorporation by coprecipitation into WZ enhances the paraffin isomerization activity of these catalysts showing that the acid sites of these solids are strong enough to perform the isomerization reaction even by the monofunctional mechanism. However, none information about the specific role of iron as a promoter was provided. Additionally, Wong et al. [12] verified an additional cooperative role of iron promoter in the doubly promoted Pt/FWZ catalyst prepared by impregnation. They suggest that highly dispersed Fe<sup>3+</sup> species promote *n*-butane isomerization reaction through a redox effect for the generation of Brønsted acid sites. It has been also proposed that the promoting effect of Fe is a combination of various effects such as the decoration of platinum by iron oxide or allowance of the migration of activated species; but in general, several studies have suggested a role as redox initiator for WZ catalysts containing Pt and Fe as promoters [10,11].

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