Nature of the active sites of promoted tungstated zirconia catalysts

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Abstract

A series of tungstated zirconia (WZ) catalysts doped with iron or manganese was synthesized by coprecipitation. The samples were impregnated with platinum and evaluated in the n-hexane isomerization. The catalysts were characterized by XRD, Raman spectroscopy, XPS, HRTEM and HAADF-STEM. It was found that the incorporation of these promoters modifies the reducibility of the Zr-WO_x clusters, modifying the nanostructure, but not the domain size of these clusters, yielding higher catalytic activity. Some evidences of the formation and identification of the catalytic species at atomic level, by direct observation of tungsten oxide structures atom by atom in this system are discussed.

Keywords: Promoters, Subnanometric Zr-WOx Clusters, n-Hexane Isomerization.

1. Introduction

Solid acid catalysts play an important role in several chemical processes, such as alkanes isomerization, catalytic cracking, esterification and transesterification, acetylation of alcohols and phenols, dehydration of alcohols and alkylation reactions. Among these acid systems, tungstated zirconia oxides (WO_3-ZrO_2) have received significant attention due to their catalytic properties, which come mainly from their acidic features. It is generally accepted that the catalytic activity of the WZ catalysts arises from the formation of well-dispersed WO_x-ZrO_x clusters[1-3]. Wachs and col.[2] have proposed that these clusters are ~1 nm in size. Iglesia and col.[1] pointed out that exists a correlation between the domain size and the catalytic activity. However, it is common that samples with the same domain sizes and with the presence of well-dispersed WO_x-ZrO_x clusters present a very different catalytic activity. Thus, in this work we synthesized WZ samples with the same conditions (tungsten content and calcination temperature) in order to obtain catalysts with the same domain size, and promoted with different contents of iron and manganese. We showed the relevance of the reducibility of these samples, induced by the presence of the dopants (Fe, Mn), in the formation of the catalytic sites for the n-hexane isomerization reaction, as well as some evidences of the formation and identification of the catalytic species at atomic level.

2. Experimental

The Fe- or Mn-promoted ZW catalysts (15 wt% WO_3) were prepared by surfactant-assisted coprecipitation similar to the procedure described previously[3]. Briefly, zirconia, tungsten and the promoter precursors in aqueous solutions were coprecipitated with the surfactant using NH_4OH. The precipitates were aged in their mother liquor at 80 °C for 16 h, washed and dried at 110 °C for 24 h. Calcination treatment was performed in static air at 700 °C for 4 h. Finally, the samples were impregnated with Pt (0.3 wt%) with $H_2PtCl_6{\cdot}6H_2O$, followed by dried at 110 °C and calcined at 300 °C in static air for 3 h. The catalytic activity was measured in the n-hexane isomerization reaction in a Combinatorial Multi Channel Fixed Bed Reactor (MCFBR) (Symyx). Pretreatment 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-C_6=1.47 molar ratio. The reaction was conducted at 260 °C, 0.689 MPa, 3.7 h^{-1} WHSV and using a mixture of 100 $cm^3 min^{-1}$ of H_2 and 0.4 $cm^3\ min^{-1}$ of n-hexane.

3. Results and discussion

Figure 1 show the similarity of the samples in nanostructure and domain size, evaluated by XRD, UV-vis DRS and Raman. Then, the type of WO_x species developed over the samples may explain the differences in the catalytic activity (Table 1). The results also indicate the redox effect of these cations (Fe, Mn), as it was found by XPS (Figure 2). HAADF images show the WO_x species as bright spots supported over ZrO_2.

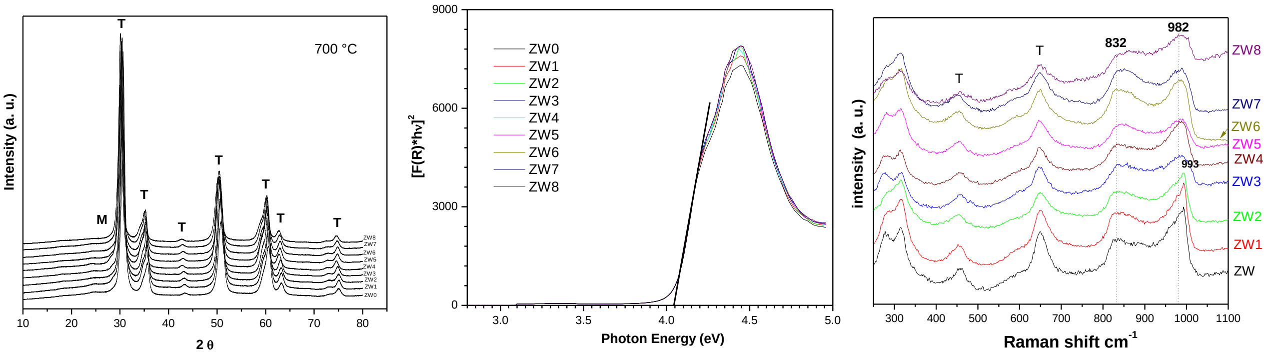

Figure 1. XRD, UV-vis and Raman spectra of the Pt/WO_3-ZrO_2 catalysts doped with different contents of Fe and/or Mn.

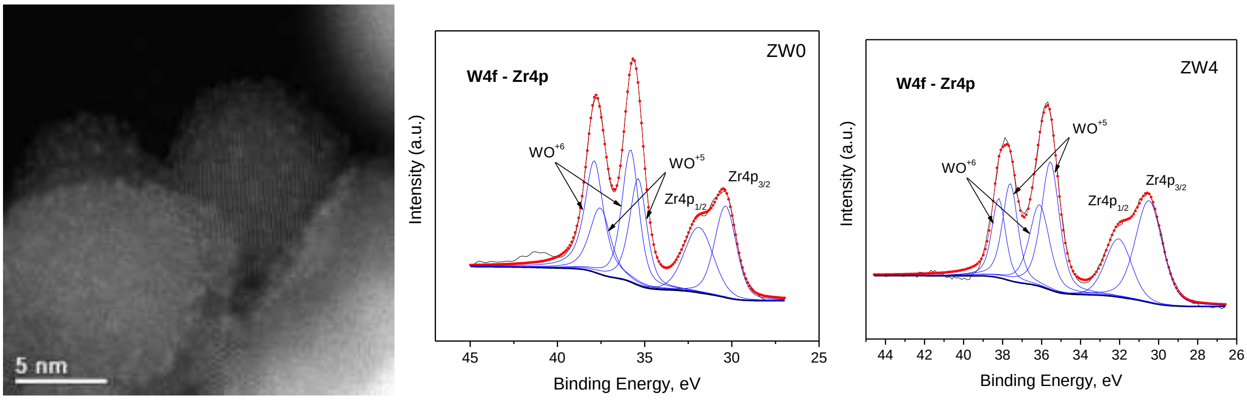

Figure 2. Typical HAADF-STEM image, XPS spectra of the blank (ZW0) and the most active sample (ZW4).

Table 1. Composition, conversion and products distribution in the n-hexane isomerization reaction at 260 °C.

Catalyst	%wt Fe	%wt Mn	X_A (% mol)	Selectivity (% mol)				
				2 MP	3 MP	2,2 DMB	2,3 DMB	Cracking
ZW0	0	0	56.1	50.5	33.5	4.1	11.9	0
ZW1	0.5	1	71.6	47.0	31.0	8.0	12.5	1.5
ZW2	1	0	66.5	48.1	31.9	6.6	12.4	0.5
ZW3	0	0.5	71.6	48.5	31.9	6.6	12.5	1.0
ZW4	0	1	71.9	48.4	31.8	6.8	12.5	0.5
ZW5	0.5	0.5	64.8	49.2	32.2	6.2	11.9	0.5
ZW6	0.5	1	61.3	48.8	32.1	5.0	12.2	1.9
ZW7	1	0.5	62.9	48.5	32.1	5.4	12.1	1.9
ZW8	1	1	54.8	49.8	33.4	3.8	12.7	0.3

4. Conclusions

It was observed a promotional effect in ZW samples with low content of dopants. It was confirmed that the most active sites in this catalysts are subnanometer-three-dimensional WO_x clusters that contain some zirconium cations. These results also indicate the redox effect of these cations as it was found by XPS.

References

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