Study of catalytic nanomaterials of Pt/ZrO_2-WO_3 and Pt/ZrO_2-TiO_2-WO_3 synthesized by Non-Alkoxides Sol-Gel route for hydroisomerization of alkanes

J. Vera-Iturriaga[a], M. L. Hernández-Pichardo[a,*], J. A. Montoya de la Fuente[b]
[a] Laboratorio de nanomateriales sustentables, Instituto Politécnico Nacional, ESIQIE, Av. IPN S/N Zacatenco, CDMX, Gustavo A. Madero, 07738, México.
[b] Gerencia de refinación de hidrocarburos, Instituto Mexicano del Petróleo, Eje central Lázaro Cárdenas 152, CDMX, Gustavo A. Madero, 07730, México.
**Corresponding author: mhernandezp@ipn.mx, +52 55 9175 8375*

Abstract: Two series of supports were synthesized by Non Alkoxides Sol-Gel route. The ZrO_2-WO_3 and ZrO_2-TiO_2-WO_3 supports were modified with tungsten loads of 15 and 20 wt%, afterwards two different calcination temperatures were used (700 and 800 °C) and finally some samples were added with hydrogen peroxide to observe its effect on the supports. Only in ZrO_2-TiO_2-WO_3 was added with 3 wt% of titania. Wet impregnation was used for the Pt impregnation of all materials. Catalysts were characterized by XRD, Raman, XPS, TPR. The catalytic evaluation was performed on the n-hexane isomerization. ZW20SG-H7 sample presented the higher catalytic activity and selectivity.

Keywords: Non alkoxide synthesis, tungstated zirconia, alkane isomerization.

1. Introduction

Isomerization process produces branched alkanes which are added to the gasolines pool increasing the octane number, becoming important in motor fuels production. Although there are active catalysts for these processes like Pt/HCl-Al_2O_3 and Pt/H-mordenite, these catalysts present some problems as stability and high operation temperatures. Thus, in this work the use of tungstated zirconia is proposed as solid support. Despite this support is well known like active material for alkane isomerization, with highly selective and thermally and mechanically stable, this samples prepared by conventional methods are still does not active enough like the commercial catalyst. With the modification of the Sol-Gel method by non-alkoxide route, it is expected that a support with a high acidity and high concentration of Brönsted-Lewis sites is generated, furthermore presenting polytungstates, clusters and Zr-O-W bonds, that are responsible to isomerize and restructure the alkane to isomers. The presence of the mentioned structures facilitates spillover effect and increasing SMSI in all material, in addition to facilitating the platinum reduction. This result is expected, because this modification of Sol-Gel process control the hydrolysis reaction and generates uniform particle size, obtaining the WO_x structures necessary to generate carbonium ion, generating mono and branched alkanes on the catalyst surface.

2. Experimental

ZrO_2-WO_3 was prepared by Sol-Gel Non-Alkoxide method, where an aqueous solution zirconium oxychloride was mixed with ammonium metatungstate. The solution was stirred for 10 min. Then etanol, propilene oxide and finally hydrogen peroxide was added dropwise. Hydrogen peroxide was added in some samples to observe its effect in the synthesis. The tungsten loads were 15 and 20 wt%, and only for ZrO_2-TiO_2-WO_3 support 3 wt% of TiO_2 was added, using titanium butoxide like precursor. Afterwards all materials were aged for 48 h and they were dried and calcined at 700 and 800 °C. Pt was added via wet impregnation with chloroplatinic acid dissolved in ethanol. The Pt (0.3 wt%) containing catalyst was dried at 120 °C for 1 h, then calcined at 350 °C for 2 h.

3. Results and discussion

Figure 1 shows the Raman spectrum of sample ZW20SG-H7. The Raman band at 580 cm^{-1} is attributed to Zr-O-W bonds that indicates higher acidity in support, facilitating SMSI [1]. Moreover, this spectrum also shows the characteristic bands at 1000 cm^{-1}, 260 cm^{-1} and 472 and 640 cm^{-1} corresponding to W=O, W-O-W bonds, tetragonal zirconia structures [1]. Figure 2 shows, XRD diffraction patterns of

ZW20SG-H7 sample. Tetragonal ZrO_2 was observed with the main sharp peaks at *2θ= 30.2°, 35.2°, 50.2°, 60.2° y 62.8°*. Also, monoclinic tungsten was observed an XRD pattern with the main sharp peaks at *2θ= 23.1°, 23.5° y 34.3°*. Figure 3 shows, Brönsted-Lewis acid sites of ZW20SG-H7 sample and this sample shows an acid sites increment (Table 1). This can be attributed to the incorporation of hydrogen peroxide. Figure 4 shows the activity of tungstated zirconia catalyst synthesized by Sol-Gel Non-Alkoxide method vs coprecipitation method. Resulting more active the catalyst synthesized by Sol-Gel. Figure 5 shows, selectivity of catalyst synthesized by both methods.

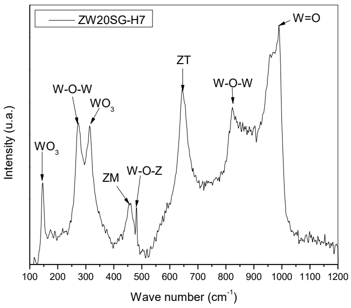

Figure 1. Laser Raman spectra in the 100-1200 cm^{-1} range of ZW20SG-H7. Band 480 cm^{-1} corresponding to Zr-O-W bonds.

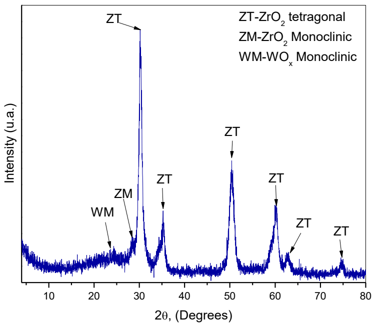

Figure 2. XRD diffraction pattern of ZW20SG-H7 sample.

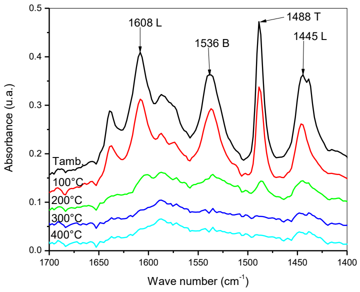

Figure 3. FTIR-Py spectra in the 1400-1700 cm^{-1} range of ZW20SG-H7 sample.

Temperature (°C)	Brönsted acid sites (μmol/g)	Lewis acid sites (μmol/g)	Total acid sites (μmol/g)
50	149	136	285
100	116	76	12
200	24	36	60
300	2	4	6
400	0	0	0

Table 1. Acid sites Brönsted-Lewis and totals of ZW20SG-H7 sample.

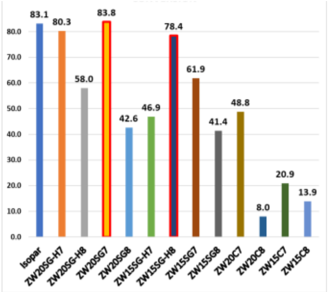

Figure 4. Activity of Sol-Gel catalysts vs coprecipitation method.

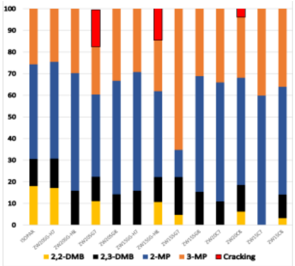

Figure 5. Selectivity of Sol-Gel catalysts vs coprecipitation method

4. Conclusions

The addition of hydrogen peroxide, tungsten loading (20 wt%) and calcination temperature play a significant role on the nature of tungsten oxide species present in the surface of the zirconia. This was determined, since the addition of hydrogen peroxide increased the acid sites in surface of catalyst, while calcination at 700 °C generated the suitable nanostructures to isomerize alkanes. Structures like tetragonal ZrO_2, Zr-O-W, W=O that can see in Figure 1 and possibility of cluster structures for slow intensity in XRD patterns. Furthermore, this work shows that this modified Sol-Gel approach produces more active catalysts for this reaction, compared with materials synthesized by conventional methods. ZW20SG-H7 sample presented the higher catalytic activity and selectivity, even superior than to the commercial sample.

References

[1] G. Valavarasu, B. Sairam, *Pet. Sci. Technol.* Vol. 31, (2013), p. 580–595.
[2] M.L. Hernandez-Pichardo, J.A.M. De, P. Angel, A. Vargas, C. Reza, *Catal. Commun.* Vol. 10, (2009), p. 1828–1834.
[3] Y. Ono, *Catal. Today*, Vol. 81 p. 3–16, 2003.
[4] W. Zhou, N. Soultanidis, H. Xu, M.S. Wong, M. Neurock, C.J. Kiely, I.E. Wachs, Acs. Catal. Vol. 150, (2017) p. 1-17.
[5] C.D. Baertsch, K.T. Komala, Y. Chua, E. Iglesia, *Catal. Today*, Vol. 57, (2002), p. 44–57.
[6] C.N. Chervin, B.J. Clapsaddle, H.W. Chiu, A.E. Gash, J.H. Satcher, S.M. Kauzlarich, Acs Catal. Vol. 60, (2006), p. 1-9.