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

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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 ºC) 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$_2$O$_3$ 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 ºC. Pt was added via wet impregnation with chloroplatinic acid dissolved in ethanol. The Pt (0.3 wt%) containing catalyst was dried at 120 ºC for 1 h, then calcined at 350 ºC 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 20 = 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 20 = 23.1°, 23.5° y 34.3°. Figure 3 shows, Brønsted-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 tungstate 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.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Brønsted acid sites (μmol/g)</th>
<th>Lewis acid sites (μmol/g)</th>
<th>Total acid sites (μmol/g)</th>
</tr>
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<tbody>
<tr>
<td>55</td>
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<td>139</td>
<td>288</td>
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<tr>
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<tr>
<td>400</td>
<td>0</td>
<td>0</td>
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</tr>
</tbody>
</table>

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

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