Effect of synthesis parameters on NiWS supported catalysts in the hydrodesulfurization of 4,6 dimethyldibenzothiophene

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Introduction

Hydrodesulfurization (HDS) of diesel has been the scope of most of the studies published in recent years due to its increasing demand [1]. NiW sulfides are not often employed in hydrotreating because of cost reasons [1]. They are however an important ingredient in hydrocracking catalysts due to their high hydrogenation activity. Thus, several groups have demonstrated that NiW sulfide based hydrotreating catalysts bring some advantages in the conversion of alkylated dibenzothiophenes molecules [2]. In previous works, Zirconia-based mixed oxides have shown prominent catalytic properties due to its ability to disperse active phase. Furthermore, catalysts supported on titania-zirconia are known for their great catalytic activity compared with conventional NiW/Al2O3 systems.

Unlike alumina-supported materials, W reduction takes place in two stages when supported on Titania-based mixed oxides. [3]. The first corresponds to the partial stabilization of tungsten monoxide, after that the reduction continues to form the monoxide corresponding to the W2+ state of the metal. The aim of this work was to understand the correlation that exists between the reduction path followed by tungsten species in a NiW-TZ catalyst and their activity in deep desulfurization. The influences of metal loading and support composition were investigated.

Materials and Methods

A Titania-Zirconia support with 40%wt. of titania (4TZ) was synthesized by the sol-gel method. Zirconium propoxide (70% Aldrich) and titanium iso-propoxide (97% Aldrich) were used as precursors. The nominal molar ratios of reactants in sol-gel synthesis were: alcohol:water:acid:alcoxide = 65:30:0.05:1. A 60% titania mixed oxide was also prepared using the same method. NiW catalysts were prepared by sequential incipient wetness impregnation so that the tungstate loadings at the end of the synthesis were 15%wt., 25%wt., and 35%wt. for the 4TZ support and 25%wt. for the 6TZ support. Ammonium metatungstate (Aldrich) and Nickel nitrate (Aldrich) were used as metal precursors. After impregnation, the catalysts were dried in air at 130°C for 4 h and sulfided with a flow of 10 %mol H2S/H2 mixture at 400 °C for 4h. Catalytic activity for 4,6 dimethyldibenzothiophene (DMDBT) HDS was measured in a batch reactor at 320°C and 800 psi of H2. A Micrometrics TPD/TPR 2900 apparatus was used to perform Temperature programmed reduction tests using a TCD detector were performed on the oxide WOx and NiOx samples. The carriers were also characterized by this technique as references. A Jeol 2100 F electron microscope equipped with an EDS detector was used to characterize the sulfides samples.

Results and Discussion

When comparing catalytic activities for the different catalysts supported on 4TZ and 6TZ, the catalyst loaded with 25% of tungsten supported on 4TZ presented the highest activity. For the catalysts with 15% and 35% W loading, the activity was lower. TPR studies revealed that the reduction of TZ supported NiW catalysts exhibited three important stages: the reduction on Ni species at 450°C followed by two peaks which correspond to the tungsten reduction at ca. 700°C and 850°C, as summarized in Table 1. Theoretically, the hydrogen consumption must be equal for each band, however a variation between the intensity of the peaks lead us to consider an incomplete reduction for one of the stages. This was plotted versus the activity for the different catalysts (Fig. 1) versus the ratio between the hydrogen consumption in each reduction stage for each catalyst. A volcano like curve was formed with a maximum near to a R1/R2 ratio of 1. This can be interpreted in terms of a relationship between the reduction path of the tungsten species and the sulfidation of the active phase prior to the reaction. Furthermore, it is necessary for a highly active catalyst that tungsten reduces through a two-step route, as pointed out by Vermaire et al. [3]. Sulfidability of tungsten species could be closely related to their reduction ability. Therefore, a reduction at low temperature, as the one which occurs in various steps, can lead to a higher grade of sulfidation of tungsten. Chemical analysis obtained from EDS results agreed with the differences in sulfidation degree deduced from TPR results.

Table 1. Reduction stages measured on catalysts NiWx

<table>
<thead>
<tr>
<th>Reaction with H2</th>
<th>Temp (°C)</th>
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<tbody>
<tr>
<td>First reduction (R1)</td>
<td>WO3 → WO2</td>
</tr>
<tr>
<td>Second reduction (R2)</td>
<td>WO2 → WO</td>
</tr>
</tbody>
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Figure 1. Hydrogen consumption ratio versus activity in HDS of DMDBT

Significance

The knowledge about sulfidation of active phase NiWS and the factors which are involved in the process are important to deeply understand the variations in HDS activities.

References