Deep Hydrodesulfurization Over Novel Trimetallic NiMoW Catalysts Supported on SBA-15

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Introduction
In the last decade, to comply with new environmental legislation worldwide, it has been necessary to increase the production of ultra low sulfur diesel (ULSD). This objective can be reached by designing of more active or selective hydrodesulfurization (HDS) catalysts than the traditional (Co,Ni)Mo/Al₂O₃ one. It is well-known, that catalytic performance of HDS catalysts can be modified by changing the nature of the support or the active phase. In this line, well-ordered mesoporous molecular sieves of the SBA-15 type have already been tested as supports for HDS catalysts giving good results [1]. On the other hand, a new generation of bulk hydrosprocessing catalysts was developed for the production of ULSD [2]. The commercial bulk NiMoW catalyst (NEBULA) is at least three times more active than the alumina-supported HDS catalysts, which was attributed to the formation of a new mixed NiMoW active phase, better than the conventional bimetallic Ni-(Mo,W)ₓS and Co-Mo-S counterparts. However, high metal content makes bulk catalysts expensive. Regarding supported trimetallic catalysts, up to now, there are only few reports about supported NiMoW catalysts for HDS [3].

Materials and Methods
In the present work, a series of trimetallic catalysts supported on SBA-15 were prepared using citric acid (CA) and adjusting pH of the impregnation solutions to basic (9) or acid (1) values (NiMoW-CA(9) and NiMoW-CA(1) catalysts). A reference trimetallic catalyst (NiMoW) was prepared without addition of CA. SBA-15 support was synthesized according to a well-known procedure [4]. All NiMoW/SBA-15 catalysts were prepared by incipient wetness co-impregnation of aqueous solutions of Ni(NO₃)₂·6H₂O, (NH₄)₂MoO₄·4H₂O and (NH₄)₂H₂W₁₈O₆₉·18H₂O. After impregnation, samples were dried (100 °C, 24 h) and calcined (500 °C, 4 h). The nominal composition of the oxide catalysts was 4·10⁻² mol/g of MoO₃ and NiO. Support and catalysts were characterized by nitrogen physisorption, XRD, UV-vis diffuse reflectance spectroscopy (DRS), temperature programmed reduction (TPR), SEM-EDX and HRTEM. The dibenzothiophene (DBT) and 4,6-dimethyl dibenzothiophene (4,6-DMDBT) HDS activity tests were performed in a batch reactor at 300 °C and 7.3 MPa total pressure for 8 h. Prior to the catalytic activity evaluation, the catalysts were sulfided ex-situ at 400 °C for 4 h in a stream of H₂S in H₂. The course of the reaction was followed by withdrawing aliquots each hour and analyzing them by gas chromatography.

Results and Discussion
Nitrogen adsorption-desorption isotherms of SBA-15 and trimetallic catalysts were of type IV with a H1 hysteresis loop. Results from the textural characterization of NiMoW catalysts (Table 1) showed that they had lower values of surface area and pore volume than the SBA-15 support. Small-angle XRD showed that the characteristic pbnm hexagonal pore arrangement of the SBA-15 support was preserved after catalysts preparation. Powder XRD of trimetallic catalysts prepared with CA pointed out a good dispersion of all metal oxide species, whereas some agglomeration of MoO₃ and WO₃ species was observed in the reference NiMoW catalyst prepared without CA. DRS and TPR characterizations showed that a mixture of Mo and W oxide species in octahedral (Oh) and tetrahedral (Td) coordination were present in all catalysts. Four signals were observed in the TPR profile of the NiMoW catalyst (at 397, 481, 601 and 760 °C) in contrast, only two reduction peaks were observed for the NiMoW-CA catalysts (at 416 and ~740-770 °C).

<table>
<thead>
<tr>
<th>Sample</th>
<th>S BET (m²/g)</th>
<th>V pore (cm³/g)</th>
<th>Conversion at 8 h (%)</th>
<th>DBT</th>
<th>4,6-DMDBT</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15</td>
<td>817</td>
<td>1.07</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>NiMoW/SBA-15</td>
<td>567</td>
<td>0.76</td>
<td>82</td>
<td>57</td>
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<td>NiMoW-CA(9)/SBA-15</td>
<td>434</td>
<td>0.63</td>
<td>88</td>
<td>77</td>
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<tr>
<td>NiMoW-CA(1)/SBA-15</td>
<td>585</td>
<td>0.76</td>
<td>99</td>
<td>93</td>
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</tbody>
</table>

Trimetallic NiMoW-CA catalysts prepared with citric acid showed higher catalytic activity in HDS of both sulfur compounds tested (DBT and 4,6-DMDBT) than the reference NiMoW catalyst (Table 1). Especially high HDS activity was shown by the NiMoW-CA(1) catalyst prepared from acid impregnation solution. Its activity was almost twice higher than that of the reference NiMoW sample (Figure 1). Results from the characterization of Mo and W species in their oxide and sulfided form (TPR, HRTEM), as well as HDS results confirmed that the characteristics of Mo and W species in trimetallic catalysts prepared with CA were different from those in the NiMoW formulation.

Significance
NiMoW catalysts supported on SBA-15 were prepared for the first time with the addition of citric acid, characterized and tested in simultaneous HDS of DBT and 4,6-DMDBT. NiMoW-CA(1)/SBA-15 catalyst showed the highest activity in HDS for both DBT’s molecules tested.

References