Effect of Sodium Content on the Behavior of NiMo Catalysts Supported on Titania Nanotubes in Deep Hydrodesulfurization

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Introduction

Nowadays, the demand for high quality low sulfur transportation fuels is growing due to the necessity to solve environmental problems induced by SOx emissions. Traditionally sulfided NiMo/Al2O3 catalysts have been widely used for hydrotreatment of oil fractions. However, alumina-supported catalysts are not active enough for the elimination of low reactive sulfur-containing molecules from gas oil fractions. Because of this, the interest in new catalysts with superior performance has grown enormously [1]. Efforts have been aimed at designing more active catalysts for deep hydrodesulfurization (HDS). Among different supports for HDS catalysts, titania has attracted special attention, since Mo/TiO2 catalysts show a significantly higher intrinsic HDS activity than the alumina-supported counterparts. Nanotubular titania has already been tested as a support for CoMo-based HDS catalysts [2]. In the present work, a series of NiMo catalysts supported on titania nanotubes (TNT) were prepared and tested in dibenzothiophene (DBT) hydrodesulfurization. The aim of this study was to inquire on the effect of sodium content in the nanotubular support on the activity and selectivity of NiMo/TNT catalysts in deep HDS.

Materials and Methods

Titania nanotubes with different sodium contents were synthesized by alkaline hydrothermal treatment of commercial titania [3] followed by ion exchange with HCl solutions and drying at 120 °C for 12 h. NiMo catalysts were prepared by incipient wetness co-impregnation of aqueous solutions of nickel nitrate, ammonium heptamolybdate and citric acid. After impregnation, catalysts were dried (100 °C, 12 h) and calcined (350 °C, 2 h). The nominal composition of the catalysts was 12 wt. % of MoO3 and 3 wt. % of NiO. The catalysts will be denoted as NiMo/TNT(x), where x represents wt. % of sodium in the TNT support. The supports and catalysts were characterized by nitrogen physisorption, XRD, UV-vis DRS, TPR, SEM-EDX and HRTEM. Dibenzothiophene 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 GC.

Results and Discussion

Results from the textural characterization of supports and NiMo catalysts show that samples with large differences in the textural properties were obtained (Table 1). Surface area and pore volume of the catalysts increased, with a decrease in the support Na content. XRD characterization showed that a decrease in the supports’ sodium content was accompanied by a progressive transformation of Na2Ti6O13 into H2Ti3O7. XRD patterns of NiMo/TNT(x) catalysts pointed out a good dispersion of Mo and Ni oxide species in all catalysts. DRS and TPR characteristics of NiMo/TNT(x) catalysts showed that sodium content strongly affects the characteristics of the deposited Mo oxide species, principally Mo6+ coordination state and the ease of reduction. As a consequence, the morphology of the sulfided Mo6+ active phase was also influenced by the chemical composition of the TNT support, which in its turn affected activity and selectivity of the catalysts in dibenzothiophene HDS (Table 1). Catalysts supported on TNT with high sodium contents showed low catalytic activity, but very high selectivity towards the direct desulfurization of DBT leading to a biphenyl product. On the contrary, low-sodium content titan ia nanotubes resulted in more active NiMo catalysts with higher hydrogenation ability. A clear relationship was observed between the support’s sodium content and activity and selectivity of the NiMo/TNT catalysts in deep HDS (Figure 1).

Table 1. Textural characteristics, activity and selectivity of NiMo/TNT(x) catalysts in HDS of DBT

| Catalyst | \( \frac{S_{BET}}{m^2/g} \) | \( \frac{V_\phi}{cm^3/g} \) | DBT conv. (%) | HYD/DDS ratio
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<tbody>
<tr>
<td>NiMo/TNT(5.4)</td>
<td>114</td>
<td>0.39</td>
<td>58</td>
<td>0.09</td>
</tr>
<tr>
<td>NiMo/TNT(3.2)</td>
<td>144</td>
<td>0.43</td>
<td>78</td>
<td>0.37</td>
</tr>
<tr>
<td>NiMo/TNT(1.3)</td>
<td>166</td>
<td>0.51</td>
<td>86</td>
<td>0.73</td>
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<tr>
<td>NiMo/TNT(0.1)</td>
<td>183</td>
<td>0.56</td>
<td>93</td>
<td>1.13</td>
</tr>
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</table>

a) HYD/DDS ratio was determined as the ratio of principal desulfurized products of each route, (CHB+BCH)/BP, at 50 % of DBT conversion. CHB, cyclohexylbenzene; BCH, bicyclohexyl; BP, biphenyl.

Fig. 13. Effects of sodium content on the activity and selectivity of NiMo/TNT(x) catalysts.

Significance

NiMo catalysts supported on titania nanotubes with different sodium contents were prepared, characterized and tested in HDS of DBT. It was shown that sodium content in the nanotubular support is an important factor which determines HDS activity of NiMo/TNT(x) catalysts and their hydrogenation/hydrogenolysis abilities.

References