The structure of a novel unsupported WMoNi hydrotreating catalyst

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A novel unsupported trimetallic hydrotreating catalyst was investigated to determine its structure in the oxidic as well as in the sulfided form. The oxidic catalyst precursor was prepared via coprecipitation using aqueous solutions of ammonium heptamolybdate, ammonium-metatungstate and nickel nitrate. The metal content in the sample is 38 wt.% W, 10 wt.% Mo and 21 wt.% Ni.

The sulfidation was followed in situ by quick XAFS measurements at the Mo K-edge (20000 eV, Figure 1, left) and the Ni K-edge (8333 eV, Figure 1, right). The activation was carried out in 10 % H₂S in H₂ from the room temperature to 400 °C with a heating rate of 5 °C/min.

At the room temperature the XANES of at the Mo K-edge showed a pre-edge peak at around 19995 eV, which is characteristic for distorted octahedrally coordinated Mo (+VI) in oxidic WMoNi species. Additionally a broad signal around 20030 eV was observed beyond the absorption edge. During sulfidation the fine structure changed indicating the coexistence of oxygen and sulfur neighbours in the temperature range between 142 and 274 °C. At 274 °C the pre-edge feature disappeared due to the reduction of Mo +VI to +IV. At the Ni K-edge a small pre-edge feature was observed at 8330 eV for the oxidic WMoNi catalyst precursor, indicating a tetrahedral or distorted octahedral Ni coordination. Moreover, the intense white line at 8350 eV is characteristic for Ni (+II). Above 200 °C the intensity of the white line was rapidly decreasing due to the replacement of oxygen by sulfur. Additionally, the absorption edge moved to lower energy and the intensity of the pre-edge was increasing, which indicates a higher coordination symmetry. At the W LIII-edge (10207 eV) the XANES of the oxidic WMoNi showed a very intense white line, which indicates W (+VI). Sulfidation was observed at temperatures above 300 °C by the decrease of the intensity of the white line.

The EXAFS of the oxidic precursor and the sulfided catalyst analysed with VIPER are shown in Figure 2.
Figure 2: Fourier-transforms of oxidic (upper line) and sulfided WMoNi (bottom line) at the Mo K-edge (1a, 1b), Ni K-edge (1b, 2b) and the W LIII-edge (1c, 2c).

The structural parameters of the samples determined by fitting the oscillations in k space are summarized in Table 1.

The distance of first Mo-S shell is equivalent to MoS$_2$ [6,7,8], but the coordination number was lower. Consequently, Mo in WMoNi is less sulfided than in bulk MoS$_2$. The Mo atoms were surrounded by W and Mo at almost the same distance and by Ni but all these neighbours appear with low coordination numbers.

Table 1: Structural parameters resulting from Mo K-edge $k^2$ weighted FT EXAFS function of sulfided WMoNi; (a) Debye-Waller factor, (b) Inner-potential correction.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Shell</th>
<th>R, Å</th>
<th>CN</th>
<th>$\Delta \sigma^2$, 10$^{-2}$ Å$^2$ (a)</th>
<th>$\Delta E_0$, eV (b)</th>
<th>Fit parameter</th>
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<tbody>
<tr>
<td>WMoNi</td>
<td>Mo-S</td>
<td>2.41</td>
<td>4.71</td>
<td>0.37</td>
<td>8.13</td>
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<td></td>
<td>Mo-W</td>
<td>3.15</td>
<td>1.83</td>
<td>0.28</td>
<td>-0.09</td>
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<td>Mo-Mo</td>
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<td>1.38</td>
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<td>7.81</td>
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<td>Mo-Ni</td>
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<td>0.6</td>
<td>0.41</td>
<td>6.06</td>
<td>2 Mo-Ni at 3.16 Å</td>
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References