**Individual and combined effects of mesoporous alumina, phosphorous and EDTA on NiMo catalyst for hydrotreating of heavy gas oil**

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**Introduction**

The oil sands bitumen derived heavy gas oil (HGO) is rich in sulfur (S) (3.7-4.2 wt.%) and nitrogen (N) (3.4-4.1 wt.%) content. The S and N content needs to be lowered before downstream catalytic processing of HGO because sulfur is known to be poisonous for catalyst. Therefore, the most widely used upgrading process is hydrotreating and the conventional catalyst used for hydrotreating is Ni or Co and Mo or W supported on γ-Al₂O₃ [1]. The ever increasing stringent environmental regulations and availability of sour crudes such as, crude from oil sands, need more active and selective catalyst for hydrotreating. From past few decades the research is focused on improving the catalytic activity by modifying support material and addition of additives such as P and B [2,3].

In this research, mesoporous alumina as support material for NiMo hydrotreating catalysts is synthesized with P and EDTA as additives. The series of catalysts were synthesized using wet impregnation method to study the individual and combined effects of mesoporous alumina, phosphorous and EDTA on hydrotreating of HGO. XANES technique was predominantly used to determine the structural changes and HRTEM was used to visualize and measure active metal dispersion. The activities are measured in terms of hydrodesulfurization (HDS), hydrogenitrogenation (HDN) and hydrodearomatization (HDA).

**Materials and Methods**

All materials were characterized using N₂-physisorption (BET), CO-chemisorption, pyridine-FTIR, H₂-TPR, NH₃-TPD, X-ray diffraction, High resolution-TEM and XANES. Moreover, all catalysts were tested for hydrotreating reactions in continuous trickle-bed reactor at industrial conditions (8.8MPa, 395 °C, Gas/oil=600:1 and 1h⁻¹ LHSV) using HGO as feedstock. The catalysts containing phosphorous were synthesized using both sequential (SI) and co-impregnation (CI) methods.

**Results and Discussion**

The HDS, HDN and HDA results for catalysts were shown in Table 1. It was observed that there is increase in HDS and HDN activity by 4 wt.% and 16 wt.% for catalyst NiMo/Meso Al as compared to that shown by catalyst NiMoP/γ-Al₂O₃. This is assigned to high metal dispersion due to large surface area and pore volume of synthesized mesoporous alumina. The addition of EDTA resulted in increasing the MoS₂ slab length and stacking degree, which led to decrease in the dispersion and negative impact on HDN and HDS activities. The catalysts’ containing both P and EDTA performed similar to those containing only EDTA (see Figure 1), however not better than NiMo/Meso Al₂O₃. The catalyst NiMoP/MesoAl₂O₃/CI containing P prepared by co-impregnation method showed the best HDS (97 wt.%) and HDN (77 wt.%) activity among all other studied catalysts. This increase in activity is attributed to the influence of P on reducibility, acidic strength, structural changes and desired dispersion.

**Significance**

The effect of EDTA depends on type of support material and extent of dispersion. In cases of fine active metal dispersion such as in NiMo/Meso Al, EDTA shows negative effects. The effect of P depends on method of addition and in this case CI method provides desired dispersion, reducibility and acidic strength thus impacting positively the HDS, HDN and HAD activities.

**Table 1: HDS, HDN and HDA activities of catalysts containing P and EDTA with HGO at 395 °C (error ± 1.0 %)**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>(HDS) wt.%</th>
<th>(HDN) wt.%</th>
<th>(HDA) wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiMo/Meso Al</td>
<td>96</td>
<td>63</td>
<td>42</td>
</tr>
<tr>
<td>NiMoP/Al(CI)</td>
<td>97</td>
<td>77</td>
<td>41</td>
</tr>
<tr>
<td>NiMoP/Al(CI)/1EDTA</td>
<td>94</td>
<td>60</td>
<td>43</td>
</tr>
<tr>
<td>NiMoP/γ-Al₂O₃</td>
<td>92</td>
<td>54</td>
<td>42</td>
</tr>
<tr>
<td>NiMoP/γ-Al₂O₃/1EDTA</td>
<td>96</td>
<td>64</td>
<td>44</td>
</tr>
</tbody>
</table>

**Figure 1: (a) Length and (b) Layer stacking distribution of MoS2 slabs in catalysts with P and EDTA**

**References**