Influence of active phase loading in hydrodeoxygenation (HDO) of ethylene glycol over promoted MoS$_2$/MgAl$_2$O$_4$ catalysts

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1. Introduction
Catalytic fast hydrolysis can be used to convert solid lignocellulosic biomass into liquid fuels by combined fast pyrolysis and catalytic hydrodeoxygenation (HDO) [1]. The advantage of this technique is that the pyrolysis vapors can be deoxygenated and stabilized against polymerization immediately when formed, since fast pyrolysis occurs in the presence of an HDO catalyst and hydrogen. Promoted MoS$_2$ catalysts are active and selective for HDO [2]. Since the cellulosic part of biomass contributes to polymerization and coking [3], a key focus of the catalyst and process development is to investigate HDO of cellulose and hemicellulose derived compounds. Ethylene glycol (EG) represents these compounds and was used as model compound in this work.

2. Experimental
Catalysts (Ni- and Co-promoted MoS$_2$/MgAl$_2$O$_4$) where prepared at different active phase loading by incipient wetness impregnation followed by in-situ sulfidation in a fixed bed reactor setup, which was also used for activity testing. In activity tests, 0.5-4.0 g catalyst was loaded into the reactor, and ethylene glycol was fed at $\approx 0.15$ mL/min giving a weight hourly space velocity (WHSV) of 2-19 gethylene/gcat h. Activity tests were run for up to 172 h at 400 °C, a total pressure of 40 barg, 27 bar H$_2$, and a co-feed of H$_2$S typically around 550 ppm. Gaseous products were quantified with GC-TCD, while liquid products and unconverted EG were quantified with GC-MS/FID. Fresh and spent catalysts were analyzed with BET, TEM, ICP-OES, XRD, and Raman spectroscopy.

3. Results and discussion
The conversion of EG over the pure MgAl$_2$O$_4$ support (WHSV = 9 h$^{-1}$) showed that it catalyzed coupling reactions such as alcohol condensation, dehydration, and acetalization. The conversion of EG over low (L, 0.8-0.9 wt% Mo) and moderate (M, 2.8-3.4 wt% Mo) loading catalysts showed that Ni- and Co-MoS$_2$ catalyzed both HDO (giving ethane and ethylene (C$_2$H$_4$)) and cracking (giving CO, CO$_2$, and CH$_4$(C$_4$)). There was a higher selectivity towards HDO as seen from the C$_2$/C$_4$ yield ratio of 1.1-1.5, independent of catalyst loading (see Table 1). The moderate loading catalysts showed superior hydrogenation activity (ethane formed rather than ethylene), whereas the low loading catalysts formed a mixture of ethene and ethane during activity tests (see Table 1). The EG conversion was $> 90\%$ for all catalysts at an EG WHSV of 2 h$^{-1}$. Catalyst deactivation was observed for the low loading catalysts (WHSV = 2 h$^{-1}$), and by increasing the WHSV, deactivation could also be observed for the moderate loading catalysts (see Figure 1). Carbon deposition was the main reason for catalyst deactivation, determined by TEM, elemental analysis and Raman spectroscopy.

4. Conclusions
Ni-MoS$_2$ and Co-MoS$_2$ supported on MgAl$_2$O$_4$ is active and selective for HDO. The MoS$_2$ based active phase catalyzes HDO, but also cracking, with a C$_2$/C$_4$ yield ratio $> 1$. The active phase loading and WHSV influences the hydrogenation reaction and the degree of deactivation.

References

Table 1. EG conversion (X) and selected carbon based yields (Y). WHSV = 2 h$^{-1}$ (for MgAl$_2$O$_4$, WHSV = 9 h$^{-1}$). TOF = 14-20 h. ETA: ethane. ETY: ethylene.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Loading [wt%]</th>
<th>X [%]</th>
<th>Y$_{ETA}$ [%]</th>
<th>Y$_{ETY}$ [%]</th>
<th>Y$<em>{C2}$/Y$</em>{C1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(L) Ni-MoS$_2$</td>
<td>Mo:0.83 Ni:0.17</td>
<td>96</td>
<td>2.5</td>
<td>8.2</td>
<td>1.3</td>
</tr>
<tr>
<td>(M) Ni-MoS$_2$</td>
<td>Mo:0.88 Co:0.16</td>
<td>100</td>
<td>44</td>
<td>0</td>
<td>1.4</td>
</tr>
<tr>
<td>(M) Co-MoS$_2$</td>
<td>Mo:3.28 Co:0.58</td>
<td>100</td>
<td>44</td>
<td>0</td>
<td>1.4</td>
</tr>
<tr>
<td>MgAl$_2$O$_4$</td>
<td>-</td>
<td>25</td>
<td>0.2</td>
<td>0.9</td>
<td>1.6</td>
</tr>
</tbody>
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