NiMo/alumina hydrosulfurization catalysts modified by saccharose.  
Effect of addition stage of organic modifier.  

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Introduction  
Ultra-low sulfur diesel (ULSD) production demands for materials of enhanced hydrosulfurizing (HDS) activity, as to that of traditional alumina-supported Ni(Co)Mo/W sulfided formulations. To that end, several approaches have been attempted, being those mainly focused on either improving dispersion and sulfidability of supported phases or in optimizing decoration of MoS2 crystals by promoter (Co or Ni). The latter could improve formation of highly active “Ni(Co)Mo(W)S” phase. Regarding using organic modifiers, the beneficial influence of chelators that could complexate aforementioned promoters has been addressed by various groups [1-2]. Conversely, the effect of non-chelating organic additives (saccharides, glycols, polymers, etc.) remains very much a matter of debate, many of the fundamental aspects behind the positive aspects of utilizing those organic still remaining obscure. The favorable effect of saccharose, non-complicating additive, on HDS properties of NiMo/Al2O3 catalysts has been previously reported [5] by our group. This work focuses in determining the stage at which the organic (SA) should be added (Ni/SA=1) during catalysts preparation, to obtain materials of enhanced organo-sulfur compounds removal activity. Studied solids were characterized by various techniques to try to explain activity trends found.  

Materials and Methods  
NiMo/Al2O3 catalysts, obtained by one-pot simultaneous impregnation (12 wt% Mo, Ni/(Ni+Mo)=0.3 mol ratio, P2O5/(MoO3+NiO)=0.2 mass ratio) were modified by saccharose (Ni/SA=1 mol ratio). Three different preparation methodologies were followed: (a) modification of already calcined (400 °C) NiMo/Al2O3 (NiMo400) by SA impregnation, NiMoI; (b) SA deposition directly onto Al2O3, previously to Ni + Mo impregnation, NiMoII; (c) simultaneous Ni-Mo-P-SA deposition, NiMoIII. Materials were characterized by N2 physisorption, X-ray diffraction (XRD), infrared (IR) spectroscopy and temperature-programmed reduction (TPR), and tested (after H2S/H2 sulfiding, 400 °C, 2 h) in dibenzothiophene (DBT) conversion (batch reactor, T=320 °C, P= 7.2 MPa, solvent: n-hexadecane). Reaction products were identified by gas chromatography (FID).  

Results and Discussion  
Surface area, pore volume and average pore diameter (S, P, and D, respectively) of various solids studied are shown in Table 1. Lower S, of NiMo400 (as compared to that of bare Al2O3) nicely corresponded to textural diminution by deposition of non-porous Ni-Mo-P phases (around 25 wt%). That suggested well-dispersed impregnated phases, as significant S, losses by partial plugging of support porous network was not observed. By XRD, no additional signals, as to those of the carrier, attributable to defined crystallization to any Ni and/or Mo phases was registered, that fact corroborating well-dispersed deposited species. For dried samples prepared with SA, IR band (at 1414 cm⁻¹) due to interactions between COO- and OH groups on Al2O3 suggested significant SA deposition over support, pointing out to competitive organic additive vs. molybdates adsorption over surface hydroxyls [3]. TPR profiles of SA-modified solids (Fig. 1) showed absence of tetrahedral MoO6 species strongly interacting with the carrier. The highest DBT HDS activity was found for the catalyst prepared by simultaneous Ni-Mo-P-SA impregnation (Fig. 2). Although biphenyl (BP) was the major product in all cases, over NiMoIII, important presence of hydroDBT’s and cyclohexylbenzene (HDBT’s and CHB, respectively) suggested existence of not fully-promoted (by Ni) MoS2 crystals.  

Table 1. Textural properties of alumina support and Ni-Mo-P impregnated materials (dried and calcined), as determined by N2 physisorption (−198 °C), from 4V/F/SBET.  

<table>
<thead>
<tr>
<th>Sample</th>
<th>SSBET (m²/g)</th>
<th>Vp (cm³/g)</th>
<th>Dp (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al2O3</td>
<td>250</td>
<td>0.51</td>
<td>8.2</td>
</tr>
<tr>
<td>NiMo120</td>
<td>223</td>
<td>0.37</td>
<td>6.6</td>
</tr>
<tr>
<td>NiMo400</td>
<td>191</td>
<td>0.38</td>
<td>8.0</td>
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</tbody>
</table>

Significance  
Catalysts of enhanced HDS activity obtained by SA addition during Ni-Mo-P impregnation could enable preparation of improved materials for ULSD production at mild conditions.  

Figure 1. TPR profile, NiMo impregnated materials prepared with and without SA.  

Figure 2. Activity (DBT HDS) of SA-modified NiMo/alumina catalysts.  

References  