Steam reforming of model tar compounds over nickel catalysts prepared from hydrotalcite precursors

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Introduction.
Biomass gasification is regarded as a promising technology in the development of a worldwide sustainable energy system. The major product in this process is a combustible gas, also called syngas. However, this syngas also contains some impurities, such as organic tars, which need to be removed before its application. Among the different strategies to remove tars from the gas, catalytic steam reforming seems to be a promising alternative from an economic and technical point of view, given that a high degree of gas purity can be attained and, at the same time, the product gas heating value is increased (Ashok, et al., 2015). Ni-based catalysts have been widely applied in the steam reforming of biomass tars due to their low cost, high activity. But one of the drawbacks of this, Ni-based catalysts is the coke deposition, that can produce a faster deactivation (Michel, et al., 2013).

By the other hand, hydrotalcite-like compounds (HTLCs) are layered double hydroxides, that can be thermal treatment to give a stable, high surface area, homogeneous mixture of oxides with very small crystal size, which by reduction results in high metallic dispersion that could contribute to reduce carbon deposition. Otherwise, It’s know that the use nickel catalyst doped with different metals can improve their performance.

In this context, the objective of this work is to study steam reforming of model tar compounds over nickel catalysts prepared from hydrotalcite precursors and doped with different metals, and comparing the activity and carbon deposition during the conversion of three different aromatics: benzene, toluene and phenol.

Material and methods.
Catalyst preparation
The general formula of hydrotalcite-like compounds HTLCs synthesized was (Ni2+,Mg2+,Co2+,Cu2+)1-x (Al3+,Fe3+,La3+)x (OH)2 (CO3)x/2 . nH2O, with x = 0.32.

The HTLCs were prepared by constant pH-controlled co-precipitation of the nitrates of metal components. An aqueous solution of Ni(NO3)2.6H2O, Mg(NO3)2.6H2O, Al(NO3)3.9H2O and another nitrates of metal components (Cu(NO3)2.3H2O, Co(NO3)2.3H2O, Fe(NO3)3.3H2O and La(NO3)3.3H2O) was added slowly by HPLC pump into a multiple stage dispersing reactor. Simultaneously an aqueous solution 2M of Na2CO3/NaOH was added slowly by HPLC pump into the same reactor. Both pumps used the same dosing rate (0.3 or 0.6 ml/min). The temperature was keeping constant at 60 °C. The pH of the solution was adjusted continuously with an aqueous solution of NaOH (2 M). The synthesis equipment is showed is in the figure 1.

Figure 1. Equipment used during the synthesis of the HTLCs.
The resulting suspension was kept at constant temperature (60 or 100 °C) for 12 h. The precipitate was filtered, thoroughly washed with de-ionized water until the conductivity of the filtrate was <0.5 mS cm⁻¹ and dried at 105 °C over night (Mette, et al., 2016). The precipitate was ground to fine powders and then calcined in air with a heating rate of 5 °C/min until 850°C and keeping in this temperature for 2 h. The obtained material was pressed to a disk, then crushed and sieved. The catalysts derived from Ni-M-Mg-Al hydrotalcite-like compounds were denoted as HTNiₓMᵧ, where x was the molar ratio of Ni and y the molar ratio of other metal (Co, Cu, Fe or La). The HTLCs synthesized are summarized in Table 1.

Table 1. Metal molar ratio of the HTLCs synthesized.

<table>
<thead>
<tr>
<th>HTLC name</th>
<th>Metals</th>
<th>Molar ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTNi52</td>
<td>Ni/Mg/Al</td>
<td>52/16/32</td>
</tr>
<tr>
<td>HTNi47Co5</td>
<td>Ni/Co/Mg/Al</td>
<td>47/5/16/32</td>
</tr>
<tr>
<td>HTNi42Co10</td>
<td>Ni/Co/Mg/Al</td>
<td>42/10/16/32</td>
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<tr>
<td>HTNi47Cu5</td>
<td>Ni/Cu/Mg/Al</td>
<td>47/5/16/32</td>
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<tr>
<td>HTNi42Cu10</td>
<td>Ni/Cu/Mg/Al</td>
<td>42/10/16/32</td>
</tr>
<tr>
<td>HTNi52Fe5</td>
<td>Ni/Fe/Mg/Al</td>
<td>52/5/16/27</td>
</tr>
<tr>
<td>HTNi52Fe10</td>
<td>Ni/Fe/Mg/Al</td>
<td>52/10/16/22</td>
</tr>
<tr>
<td>HTNi52La5</td>
<td>Ni/La/Mg/Al</td>
<td>52/5/16/27</td>
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<tr>
<td>HTNi52La10</td>
<td>Ni/La/Mg/Al</td>
<td>52/10/16/22</td>
</tr>
</tbody>
</table>

Steam reforming of toluene, benzene and phenol

Steam reforming of model compounds of tar derived from biomass was carried out using a fixed-bed reactor. The used reactants were toluene, benzene and phenol. The reactor was made of a stainless steel tube (15 mm i.d.). The reactor was divided in two zones heated at different temperature: vaporized zone where water and reactant were vaporized at 300 °C and the reactor zone heated at 800 °C. The catalyst weight was 500 mg in all the experiments. Before the experiment, the catalysts were reduced in flowing H₂ and N₂ (H₂/N₂= 100/10 ml min⁻¹) at 800 °C for 0.5 h. After the reactor was purged with N₂, reactants were supplied through the vaporizing zone. The Steam to Carbon ratio used in all experiments was S/C=3.

Results.
The structure of the catalysts before and after the catalytic use was studied by means of BET method, H₂ chemisorption, powder X-ray diffraction (XRD), temperature-programmed reduction (TPR), temperature-programmed oxidation (TPO), and transmission electron microscopy (TEM).

Discussion.
All the catalysts synthetized presented similar behavior in terms of conversion, at 800 °C. The conversion of all the model compounds was in the 63–100% range. The most reactive compound was benzene, following by toluene and phenol.

Conclusions.
The Ni-La/Mg/Al and Ni-Fe/Mg/Al catalyst showed high catalytic performance in the steam reforming of tar in terms of catalytic activity, suppression of coke deposition, and catalyst stability.

References.

