Ceria supported metal catalysts for partial oxidation of ethanol

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Introduction
Ethanol has been considered a promising renewable fuel for H₂ production since it can be manufactured from biomass and does not contribute to CO₂ emissions. Hydrogen may be generated from ethanol by different technologies: steam reforming (SR); partial oxidation (POX) and oxidative steam reforming (OSR) [1]. All of these reactions face two major drawbacks: by-product formation and catalyst deactivation. Various reaction pathways may operate depending on the conditions selected and the choice of the catalyst. Catalyst deactivation has been attributed to the deposition of carbonaceous species or sintering of the metal particles.

Recently, we reported that the support plays an important role on the product distribution obtained on POX over Al₂O₃, ZrO₂, CeO₂ and CeZrO₂ supported Pt catalysts [2]. Pt/CeO₂ and Pt/CeZrO₂ catalyst exhibited good activity and stability on POX, which was attributed to the material’s high oxygen storage capacity (OSC).

The aim of this work was to study the effect of the metal nature on the performance of ceria supported metal catalysts for the ethanol partial oxidation for hydrogen production. In addition, the nature of carbon formed was also evaluated. The reaction mechanism was investigated using diffuse reflectance infrared spectroscopy (DRIFTS) carried out under steady state reaction conditions.

Materials and Methods
CeO₂ support was calcinated at 1073 K, for 1 h. The metals (1 wt. %: Pt, Pd, Rh, Ru; 10 wt. %: Co and Ni) were added to the support by incipient wetness impregnation with aqueous solutions. The catalysts were characterized by BET, XRF, TPR, DRS, DRX and TGA. The metallic dispersion and the carbon formation were determined by TEM/SEM/EDS.

The partial oxidation of ethanol was investigated within the temperature range of 473-1073 K in a fixed bed reactor at atmospheric pressure and O₂/ethanol molar ratio of 0.5. The reaction mechanism was studied through DRIFTS and TPSR techniques.

Results and Discussion
The complete ethanol conversion was achieved at around 873K, except for Pd/CeO₂ catalyst (973K). The following order was observed for the ethanol conversion at 673K: Ni ≈ Co > Ru > Rh > Pt > Pd. Bellow 773 K, the product distributions basically comprises acetaldehyde and water. Above 773K, hydrogen and CO were the main products along with methane and CO₂. The highest hydrogen selectivity occurred at 1073K and varied between 48 % (Rh and Pd) to 35% (Ru). The product distributions obtained on a dry basis at the same level of conversion (~ 65 %) for different catalysts are presented in Table 1. Nickel based catalyst exhibited the highest hydrogen selectivity and the lowest acetaldehyde formation. In addition, the percentage of hydrogen, methane and CO was the same, indicating that ethanol decomposition is the main reaction taking place on this catalyst. On the other hand, acetaldehyde was one of the main products observed for Rh, Ru, Co and Pt catalysts. A reaction mechanism was proposed based on DRIFTS experiments. Adsorption of ethanol gives rise to ethoxy species, which can be decomposed, producing CH₄, H₂ and CO, and dehydrogenated, forming acetaldehyde. Acetaldehyde desorbs or can be further oxidized to CO₂ species. Furthermore, the acetate species previously formed can be decomposed to CH₄, CO and/or oxidized to CO₂ via carbonate species. A correlation between the product distributions and the metal nature was established based on the reaction mechanism determined by DRIFTS experiments.

Table 1. Product distributions obtained at the same level of conversion for different ceria supported catalysts for partial oxidation ethanol

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>%H₂</th>
<th>%CH₄</th>
<th>%CO</th>
<th>%CO₂</th>
<th>%Acetaldehyde</th>
<th>%Acetate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>17.21</td>
<td>8.59</td>
<td>16.79</td>
<td>30.93</td>
<td>26.23</td>
<td>0.23</td>
</tr>
<tr>
<td>Pd</td>
<td>11.55</td>
<td>25.37</td>
<td>28.13</td>
<td>19.96</td>
<td>34.55</td>
<td>0.30</td>
</tr>
<tr>
<td>Ru</td>
<td>4.02</td>
<td>6.80</td>
<td>33.65</td>
<td>19.96</td>
<td>35.40</td>
<td>0.81</td>
</tr>
<tr>
<td>Rh</td>
<td>4.99</td>
<td>11.50</td>
<td>15.27</td>
<td>30.81</td>
<td>35.40</td>
<td>2.99</td>
</tr>
<tr>
<td>Co</td>
<td>9.48</td>
<td>2.26</td>
<td>17.09</td>
<td>35.41</td>
<td>32.19</td>
<td>2.99</td>
</tr>
<tr>
<td>Ni</td>
<td>26.77</td>
<td>25.00</td>
<td>27.61</td>
<td>19.56</td>
<td>2.00</td>
<td>0</td>
</tr>
</tbody>
</table>

Figure 1: SEM image of Ni/CeO₂ and TEM image of Rh/CeO₂ spent catalysts.

Significance
Development of a highly active, selective and stable catalyst for H₂ production

References