Hemicellulose-derived chemicals: one-step production of furfuryl alcohol from xylose

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Detailed characterization of Pt/SiO₂ and ZrO₂-SO₄ catalysts.

X-ray diffraction patterns (Figure S1) indicated that the commercial sulfated zirconia is a crystalline material with tetragonal structure characterized by diffraction lines at 2θ = 30.1°, 35.2°, 50.4° and 59.9°, corresponding to the planes (111), (200), (220) and (311) respectively (JCPDS 17-0923). The Pt/SiO₂ catalyst presented a diffraction pattern typical of amorphous materials due to the commercial silica used as support.

![Figure S1. Diffractograms of ZrO₂-SO₄ and Pt/SiO₂ powder catalysts.](image-url)
Surface area, pore volume and pore mean diameter of the samples are summarized in Table S1. It is noted that both catalysts present high surface area and narrow mesopores with mean diameters between 5 - 7 nm.

**Table S1.** Surface area ($S_{\text{BET}}$), pore volume ($V_p$), average pore diameter ($d_p$), chemical composition and metal dispersion of the catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$S_{\text{BET}}$ (m$^2$/g)</th>
<th>$V_p$ (cm$^3$/g)</th>
<th>$d_p$ (nm)</th>
<th>SO$_3$ (%p/p)</th>
<th>Pt (%p/p)</th>
<th>D (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO$_2$-SO$_4$</td>
<td>137</td>
<td>0.23</td>
<td>4.7</td>
<td>4.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pt/SiO$_2$</td>
<td>207</td>
<td>0.54</td>
<td>6.8</td>
<td>-</td>
<td>0.8</td>
<td>15</td>
</tr>
</tbody>
</table>

Table S1 also presents the bulk chemical composition and metal dispersion. It can be seen that the actual metal loading is close to the nominal value considered in the catalyst preparation. The sulfur content of the sulfated zirconia is consistent with that expected for this commercial material. A low Pt dispersion was found as examined by STEM. A representative image is depicted in Figure S2.

**Figure S2.** A representative STEM image of Pt/SiO$_2$ powder catalyst.
The sulfate groups in the acid catalyst were analyzed by infrared spectroscopy. The main absorption bands were recorded within 1800 – 900 cm\(^{-1}\) range as showed in the spectrum depicted in Figure S3.

![Figure S3. Infrared spectrum of the sample ZrO\(_2\)-SO\(_4\).](image)

The band at 997 cm\(^{-1}\) corresponds to the S-O symmetrical stretching whereas the vibrations at 1047, 1138 and 1230 cm\(^{-1}\) are associated with its asymmetric mode, evidencing the existence of bidentate sulfate complexes coordinated to ZrO\(_2\), as expected for the thermal treatment applied in this sample and the SO\(_4\) concentration [1]. The absorption located at 1635 cm\(^{-1}\) may be attributed to the bending mode of water adsorbed onto the catalyst [2].

Thermal stability of those sulfate groups was evaluated by thermogravimetry coupled with mass spectrometry (TG-MS). The thermogram presented in Figure S4 shows only two events of weight loss, the first one in the range between 80 °C and 150 °C and the second at above 180 °C.

![Figure S4. Thermogravimetric analysis of ZrO\(_2\)-SO\(_4\) catalyst and evolution of water (m/z = 18), CO\(_2\) (m/z = 44) and sulfur oxides (m/z = 48 SO\(^+\), m/z = 64 SO\(_2\)^+).](image)
Based on the fragment ion profiles also displayed in Figure S4, both events can be mostly ascribed to the loss of water. A quite important remark is that no sign of sulfur-derived compounds were detected in the whole temperature range monitored. These results indicate that the commercial acid catalyst is thermally stable up to 600 °C and thus no loss of sulfate surface acid groups should occur as a consequence of any thermal treatment applied in this sample. This result is in line with the behavior that has been reported in the literature for similar modified zirconia samples [3].

A qualitative analysis of the acidic properties of the commercial sulfated zirconia was performed using pyridine as probe molecule and monitored by infrared spectroscopy. The spectra collected after thermal desorption of the weak base are shown in Figure S5 for different temperatures.

**Figure S5.** Infrared spectra of pyridine desorption at 25 °C (a), 150 °C (b), 250 °C (c) and 350 °C (d) for the sample ZrO$_2$-SO$_4$.

The bands at 1445, 1490 and 1610 cm$^{-1}$ correspond respectively to $\nu_{19b}$, $\nu_{19a}$ and $\nu_{8a}$ vibrational modes of pyridine coordinated to Lewis acid centers. The absorptions at 1490, 1545 and 1640 cm$^{-1}$, on the other hand, are associated with the pyridinium ion binding to Brönsted acid sites [4]. These data show the presence of both Lewis and Brönsted acid sites on this catalyst, which typically describe the surface of sulfated zirconia solids [4]. The evolution of the absorption bands as a function of temperature reveals only a small decrease in their intensity up to 350 °C, indicating that both type of acid sites are relatively strong.
References