Conversion of glycerol to solketal catalysed by functionalised activated carbons

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Introduction

The current worldwide dependence on a finite resource as fossil fuels has prompted the development of alternative and renewable fuels, among which biodiesel has gained prominence in recent years. Biodiesel is considered a promising substitute for the petroleum-based diesel due to intrinsic advantages including renewability, lower toxicity, biodegradability, biocompatibility and lower emission profile.1 It is estimated that the production of 100 m3 of biodiesel generates 10 m3 of crude glycerol, and the growing trend of production of this fuel causes an oversupply of glycerol and a drop in its market value.2 Viable chemical processes for the up-grading of glycerol into useful products have been investigated including acetalization of ketones or aldehydes.3 In this work, we focus on a reaction of this highlighted group, i.e. the acetalization of acetone with glycerol, for which we present a new class of highly active and selective heterogeneous catalysts consisting of acid-functionalized activated carbons.

Materials and Methods

Activated carbon (AC) was prepared by impregnating of H3PO4 73%(v/v) in olive stones (particle size 0.5-2 mm) at 357 K for 4 h, using a solution to olive stones mass ratio of 1:1 followed by a thermal treatment (activation) in a vertical glass reactor under nitrogen gas flow of 100 mL min−1 at 723 K for 2 h. The remaining activating agent (H3PO4) was removed by washing the solid with hot distilled water and then the material was allowed to dry at 373 K for 12 h. The acid treatment was carried out by stirring 10 g of AC in 100 mL of either H2SO4 18M or HNO3 15M at room temperature for 3 h. Afterwards, the material was washed by distilled water in a Soxhlet extractor and dried at 373 K for 15 h. The obtained catalysts (AC, AC-S-18 and AC-N-15) were characterized by XPS, nitrogen adsorption/desorption and Boehm titration.4 In a typical catalytic test, 0.921 g (0.01 mol) of glycerol (99%), 2.324 g (0.04 mol) of acetone and 0.132 g (0.0015 mol) of 1,3-dioxane, as GC internal standard, were weighed in a 10 mL glass vial containing 25 mg of catalyst and the mixture was stirred at 800 rpm for 6 h at room temperature. The reaction products were analyzed by gas chromatography.

Results and Discussion

The AC displays a very high specific surface area of 1550 m2 g−1, pore volume of 0.94 cm3 g−1 of which 0.55 cm3 g−1 originates from micropores and a population of acid sites of 0.60 mmol g−1, which can be related mainly to carboxylic and phenolic groups. The AC treated with H2SO4 and HNO3 display a significant increase in the population of total and strong acid sites such as carboxylic and, in case of AC-S-18, sulfonic groups (confirmed by XPS analysis)5, compared to the parent material. On the other hand, treatment with the oxidizing acids is accompanied by a decrease in the surface area and pore volume, which is more pronounced in AC-N-15. The catalytic behavior of AC, AC-S-18 and AC-N-15 was investigated by performing a kinetic study of the investigated reaction (Figure 1). The conversion of the glycerol tends to reach a plateau after 5 h of reaction achieving selectivity to solketal in the range of 90 to 96%. This experiment also underlines the superior catalytic activity of the functionalized materials compared to the untreated activated carbon, confirming the importance of carboxylic and sulfonic groups to the activity of these kinds of catalysts. The heterogeneous nature of the system was checked by Sheldon’s test [4] and the conversion of glycerol was constant after removing the catalyst (in reaction conditions) after nearly 30 min (Figure 1, dashed line).

Table 1. Textural properties and acidity of the parent and acid-treated activated carbons.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>S_BET (m2 g−1)</th>
<th>V_total (cm3 g−1)</th>
<th>V_mic (cm3 g−1)</th>
<th>Total acid sites (mmol g−1)</th>
<th>Strong acid sites (mmol g−1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>1550</td>
<td>0.94</td>
<td>0.55</td>
<td>0.60</td>
<td>0.17</td>
</tr>
<tr>
<td>AC-S-18</td>
<td>1495</td>
<td>0.83</td>
<td>0.53</td>
<td>6.52</td>
<td>0.90</td>
</tr>
<tr>
<td>AC-N-15</td>
<td>1240</td>
<td>0.64</td>
<td>0.44</td>
<td>1.88</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Figure 1. Kinetic study (solid lines) and leaching test (dashed lines) for the acetalization of acetone with glycerol catalyised by AC, AC-S-18 and AC-N-15.

Significance

The functionalized activated carbons displayed high catalytic performance, achieving up to 97% conversion of glycerol (AC-S-18) with high selectivity towards solketal under mild and environmental friendly conditions (solvent-free reaction at room temperature) and with a lower catalyst loading compared to that used for state-of-the-art heterogeneous catalysts for this reaction.

References