Acid sites in modified alumina and their catalytic performance for dehydration of fructose to selective production of hydroxymethylfurfural

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Introduction

Fructose is one of the most important carbohydrates because several furan chemical products can be obtained from it, like hydroxymethylfurfural (HMF), which is considered as a versatile chemical platform. HMF can be obtained in presence of acid catalysts, an acid alumina catalyst design was completed using an alumina mesoporous material that has a high surface area and displays an acid behavior that can be controlled. In the present study, two types of alumina: commercial (AC) and synthetic by sol-gel (AS) were bi-functionalized with thiol and sulfonic ligands, using a grafting method; their catalytic performance on fructose dehydration was evaluated.

Materials and Methods

Synthesis AS: aluminum terbutoxide was dissolved in 2-propanol at 80°C/3h. H₂O was added after this step and was stirred during 24h/25°C; this was aging for 24h/25°C, afterwards, this was dried at 80°C and calcinated at 550°C/4h. SH group (ASmT, ACMTe): 1.5g AS or AC was suspended in 50ml toluene; 0.9ml of 3-mercaptopropyl trimethoxysilane (MPTMS) was added and this was stirred for 3h. The solid was filtrated and washed (ethanol), and then dried in low vacuum (15psi) at 80°C/12h. SO₂H group (ASmTS, ACmTS): 25ml THF; 1g ASmT or ACMTe and a NaH/THF (400mg/15ml) suspension were added at -78°C. Later 1.3ml 1,3-propan sulphonate were added, the mixture was stirred 18h/25°C (N₂ atm). 50ml H₂O were added; the solid was filtrated and washed with organic solvents. It was dried in low vacuum (15psi) at 80°C/12h. Characterization: FTIR (Nicolet FTIR 6700); FTIR (Perkin-Elmer 170-SX) for pyridine (py) adsorption; TPD-NH₃ (Netzsch, STA 409-PCL); Carbon-sulfur analysis (CS-2000-Eltra); ¹³C and ²⁸Si CP/MAS NMR spectroscopy (Varian Inova de 600 MHz). Fructose dehydration: 50mg catalyst, 1.5g fructose in H₂O (30wt%) and 3g methyl isobutyl ketone/2-butanol (7:3w/w) were placed inside a reactor at 180°C/30min. The fructose and HMF were quantified in a HP5890 series II gas chromatograph/flame ionization detector.

Results and Discussion

Table 1 showed the catalytic activity, fructose conversion, selectivity towards HMF and sulfur percentage in the fresh catalysts. The selectivity towards HMF can be related with the sulfur loading. There is very low selectivity for the catalysts that lacked sulfur; however, the presence of this functional group increased the catalyst selectivity towards HMF. Sulfur can be obtained from two sources: the SH or SO₂H group. It has been reported that the incorporation of SH groups promote fructose tautomerization to its furanose form, while SO₂H groups promote fructose dehydration (1). ASmTS has slightly higher sulfur content than ACmTS, but a dramatic increase on HMF selectivity. This can be explained due to a higher availability of SH groups over ASmTS than ACmTS, which can occur due to the physical and chemical properties of the alumina (2).

Table 1. Comparison of catalytic fructose dehydration by alumina catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>% Fructose Conversion</th>
<th>% HMF Selectivity</th>
<th>% Sulfur on Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>25</td>
<td>0.04</td>
<td>0</td>
</tr>
<tr>
<td>AS</td>
<td>53</td>
<td>0.37</td>
<td>0</td>
</tr>
<tr>
<td>ACmTS</td>
<td>25</td>
<td>5.2</td>
<td>4.0</td>
</tr>
<tr>
<td>ASmTS</td>
<td>72</td>
<td>55</td>
<td>5.5</td>
</tr>
</tbody>
</table>

In fig 1A, AC and AS present a signal at 3480 cm⁻¹, related with OH groups. The modified catalysts show signals at around 2848 and 2941cm⁻¹, related with the C-H bonds of MPTMS, while the signals at 1055, 1375 and 1232 cm⁻¹ are due to SO₂H (3). In fig 1B, the signals at around 1444, 1597, 1580 and 1616 cm⁻¹ are characteristic of Lewis acid sites (L); the band at 1545 cm⁻¹ (ACmTS) is related with Brønsted sites (B), and the signal at 1491 cm⁻¹ corresponds to both L and B sites (4). In fig 1C, ²⁸Si NMR spectrum confirm the bonding of MPTMS with OH groups of alumina; ¹³C confirmed the anchorage of the SO₂H over the SH group. The ACmTS and ASmTS showed the two group (SH and SO₂H) but the ACmTS showed lower concentration of SH that ASmTS; this can explain the catalytic performance.

Fig 1. A) FTIR of modified and unmodified aluminas, B) Spectra of py adsorbed to 25°C (TA) and py desorption by thermal treatment, C) Solid-state ¹³C and ²⁸Si CP/MAS NMR Spectral. Where line: black (AC), blue (AS), red (ACmTS), green (ASmTS).

Significance

Design of a catalyst that increases selectivity of HMF in fructose dehydration, by modifying acidity of alumina.

References