Valorization of carbohydrates: dehydration of sorbitol to isosorbide in the presence of acidic zeolites


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Introduction

Currently, the growing interest in the use of biomass as a renewable and sustainable raw material for the production of energy, chemicals and biofuels is driving the development of new catalytic processes and technologies for its conversion. In this context, the transformation of lignocellulosic biomass can lead to a variety of platform chemicals [1], with a broad spectrum of applications. Sorbitol is one of the useful biomass-derived chemicals that is obtained by catalytic hydrogenation of glucose, which subsequent dehydration and intramolecular cyclization in acid medium [2] gives rise to the formation of isosorbide (Scheme 1). This is a high value-added chemical widely used as intermediate in the pharmaceutical industry, additive polymers such as polyethylene terephthalate (PET) [3] and production of biodegradable polymers.

Scheme 1. Transformation of sorbitol into isosorbide

Mineral acids such as sulphuric and hydrochloric acids have efficient catalytic properties for dehydration of sorbitol [4]. However, the well-known drawbacks associated to homogeneous catalysis have promoted the studies of heterogeneous catalytic processes.

Thus, solid acid catalysts such as zeolites [5], tetravalent metal phosphates [6] and sulfated copper oxide [7] have been reported as alternative solid catalysts. Nevertheless, sometimes, drastic experimental conditions are required to reach a high catalytic activity. In the present work, different commercial zeolites, in their protonic form, have been evaluated as acid solid catalysts for sorbitol dehydration, and several experimental variables have been optimized.

Materials and Methods

The commercial NH₄⁺-zeolites have been transformed into the protonated form by calcination. Catalytic dehydration of sorbitol to isosorbide was studied in batch reactors with magnetic stirring in the absence of water, by using molten sorbitol into a silicone bath. Reaction products were identified and quantified by high performance liquid chromatography (HPLC) equipped with a multiwavelength UV-visible and refractive index detectors and a column oven.

Catalysts have been characterized by N₂ adsorption–desorption isotherms at -196°C, X-ray photoelectron spectroscopy (XPS), X ray diffraction (XRD) and temperature-programmed desorption of ammonia (NH₃-TPD).

Results and Discussion

The textural properties, as determined from the adsorption–desorption isotherms of N₂ at -196°C, have evidenced their microporous nature, inferred from the type I isotherms according to the IUPAC classification [5]. However, the hysteresis loop at high relative pressure in the case of the H-β zeolite, together with the high pore volume, reveal the existence of mesopores (Table 1).

Table 1. Textural and acidic properties of zeolites H-ZSM5, H-β and H-Y.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>S BET (m²·g⁻¹)</th>
<th>Vp (cm³·g⁻¹)</th>
<th>Surface Si/Al</th>
<th>TPD- NH₃ (µmol m⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-ZSM5</td>
<td>374</td>
<td>0.271</td>
<td>28.3</td>
<td>2.38</td>
</tr>
<tr>
<td>H-β</td>
<td>441</td>
<td>0.853</td>
<td>11.92</td>
<td>2.76</td>
</tr>
<tr>
<td>H-Y</td>
<td>595</td>
<td>0.349</td>
<td>1.36</td>
<td>2.77</td>
</tr>
</tbody>
</table>

Regarding the acidity determined from the NH₃-TPD curves, the three zeolites display high acid site density, which are higher in the case of H-β and H-Y zeolites.

Dehydration of sorbitol was conducted at 190 ºC for 6 h, by using 10 wt.% catalyst in molten sorbitol. Figure 1 compares the catalytic performance of the three zeolites. H-β zeolite attains an isosorbide yield of 55% yield, with full conversion of sorbitol. On the other hand, H-Y and H-ZSM5 zeolites showed lower sorbitol conversion, especially H-Y, and selectivities to monodehydration products.

It is necessary to take into account that after the loss of the first water molecule, the intramolecular cyclization considerably increases the steric hindrance, whereby an increase in the pore dimensions could facilitate the accessibility to the acid sites, thus improving the catalytic performance.

![Scheme 1](image-url)
The reaction was carried out at different reaction temperatures (160-210 °C) by using H-β zeolite. As can be inferred from Fig. 2, isosorbide yield is notably increased until 175ºC, and a further raising of the reaction temperature doesn’t ameliorate the catalytic activity.

The kinetic of this catalytic process was studied at 175ºC (Fig. 4). Total sorbitol conversion was achieved after 6 h of reaction, though 8 h are required to attain the highest isosorbide yield. These results are in agreement with previous reports [6-8] which suggested the conversion of sorbitol into isosorbide via sorbitan (Scheme 1).