



Feature Article

Dehydration of sorbitol to isosorbide over sulfonic acid resins under solvent-free conditions



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ABSTRACT

Different commercial sulfonic acid resins (Purolite and Amberlyst type) have been evaluated as acid catalysts for the dehydration of sorbitol to isosorbide. These acidic resins differ in their acid properties, as well as in their thermal and mechanical stabilities. Dehydration of sorbitol has been carried out under solvent-free conditions, by melting sorbitol. At the beginning of reaction, different sorbitans (monodehydration products) were detected, whose dehydration and subsequent cyclization lead to the formation of isosorbide. A maximum yield of 75% is reached after 12 h at 413 K, by using a 5 wt% of Purolite CT269, at atmospheric pressure. This resin maintains its catalytic activity after four runs, and the stability is corroborated by the negligible presence of sulphur species (coming from sulfonic acid leaching) in the reaction medium. This suitable catalytic performance can be explained by its high acid capacity (5.2 meq g^{-1}) and mechanical and thermal stabilities associated to the macroreticular structure.

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1. Introduction

Currently, much attention is being paid to the use of biomass as a renewable and sustainable feedstock for the production of biofuels, energy and chemicals [1–4]. In this regard, the biorefinery concept emerges as an alternative to the traditional refinery based on fossil raw materials (oil and natural gas), where different integrated and sustainable mechano-physical, biochemical, chemical and thermochemical processes allow biomass conversion into chemicals, biofuels and energy.

Sorbitol is one of the most important platform molecules, obtained from hydrolysis/hydrogenation of lignocellulosic biomass (mainly, from cellulose and hemicellulose) or by hydrogenation of glucose, requiring high temperature and pressure for accomplishing hydrogenation, and after subsequent filtration and refined by ion exchange, sorbitol can be finally concentrated, being employed for the synthesis of a large spectrum of chemicals [5]. Industrially, the raw material for sorbitol manufacture is glucose, usually obtained from starch [6]. Sorbitol was included as platform molecule in the revised list of top chemicals derived from biomass,

together with ethanol, furans, glycerol, lactic acid, succinic acid, hydroxypropionic acid/aldehyde, levulinic acid and xylitol [7,8].

The importance of isosorbide for the production of monomers and building blocks for new polymers and functional materials, as well as for medical and pharmaceutical uses, has been recently highlighted by Rose and Palkovits [9]. In this sense, isosorbide exhibits excellent physicochemical properties applicable to various fields of industry, since it is an important pharmaceutical intermediate (diuretic, and mainly to treat hydrocephalus and glaucoma), used as additive to improve the strength and rigidity of polymers as polyethylene terephthalate (PET), and as monomer for the production of biodegradable polymers.

Among the compounds derived from isosorbide are dinitrate and mononitrate, the latter being a compound widely used as vasodilator for angina and congestive heart failure. Isosorbide derivatives can also find potential application as fuels or fuel additives due to the high energy content, which can bring aliphatic substituents (dimethyl isosorbide (DMI)).

The dehydration of sorbitol to isosorbide occurs through two consecutive steps: a first cyclization with loss of a water molecule, which can lead to different chemical intermediates such as 2,5- and 1,5-sorbitans, considered as byproducts since they do not evolve toward isosorbide, and 1,4- and 3,6-sorbitans, whose subsequent dehydration and cyclization gives rise to isosorbide.

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This process is industrially performed under homogeneous catalysis in the presence of strong mineral acids [10,11]. Although these systems provide high sorbitol conversion at low temperature, drawbacks associated to the high costs of separation and corrosion problems in the equipment have prompted the search of alternative processes. In this context, the development of solid acid catalysts represents a more sustainable alternative from an economic and environmental point of view, and would allow a modulation of selectivity in some cases.

In this sense, various reaction systems (aqueous solution of sorbitol in gas and liquid phases, molten sorbitol) in the presence of a wide range of solid acid catalysts have been essayed. Among them, it has been reported the use of zeolites [12–15], tetravalent and trivalent metal phosphates [16–18], heteropolyacids supported on silica [19], silicotungstic acid [20], sulfated metal (Ti, Cu, Sn, Zr) oxides [21–24], niobium phosphate [25], phosphated tantalum oxide [26], and cellulose-derived solid acid catalysts [27].

Sulfonic acid resins have been also evaluated as solid acid catalysts for the conversion of sorbitol into isosorbide, and the best catalytic results have been obtained with Amberlyst-35, under different experimental conditions (molten sorbitol, sorbitol aqueous solution in gas phase) [28–31]. More recently, the catalytic performances of a commercial Amberlyst-15 and a superhydrophobic mesoporous polymer-based acid catalyst (P-SO₃-H) have been compared [32]. After 10 h at 413 K, the conventional resin showed a high conversion (94%) and selectivity to isosorbide (72%), but an isosorbide yield close to 88% at full sorbitol conversion was attained with the P-SO₃-H polymer. In addition, reutilization studies have corroborated the excellent performance and stability of the P-SO₃-H polymer, which maintained a selectivity 78% after 5 recycles, whereas the Amberlyst-15 only gave a yield of 15% after 3 recycling essays. This suitable catalytic activity of the P-SO₃-H polymer was explained by considering both its large porosity and strong hydrophobic character, which facilitate the removing of formed water molecules from the catalyst surface.

In the present work, different commercial sulfonic resins (Amberlyst and Purolite type) have been evaluated as acid catalysts for the dehydration of sorbitol to isosorbide, by using molten sorbitol. Several experimental variables have been optimized in order to achieve the highest isosorbide yield, and special emphasis was put on the reutilization study of the most active resin.

2. Materials and methods

2.1. Chemicals

D-Sorbitol (99%, Aldrich), isosorbide (Dianhydro-D-glucitol) (98%, Aldrich), 1,5-anhydroglucitol (Aldrich) and 1,4-sorbitan (USP Reference Standard) were of HPLC grade. Different commercial ion-exchange resins were studied: Purolite CT275 (P-CT275), Purolite CT269 (P-CT269) and Purolite PD206 (P-PD206), kindly provided by Purolite[®], and Amberlyst 35 (A-35) and Amberlyst 70 (A-70).

2.2. Characterization of catalysts

The textural parameters were provided by the commercial supplier. However, the nitrogen adsorption-desorption isotherms at 77 K of selected samples were obtained by using an automatic ASAP 2020 model of gas adsorption analyser from Micromeritics. Prior to N₂ adsorption, the samples were outgassed at 373 K and 10⁻⁴ mbar for 10 h. Surface areas were determined by using the Brunauer-Emmett-Teller (BET) equation and a nitrogen molecule cross section of 16.2 Å², and the Barrer-Joyner-Halenda method was used to determine average pore volume values.

X-ray photoelectron spectroscopy (XPS) studies were carried out by using a Physical Electronics PHI 5700 spectrometer equipped with a hemispherical electron analyzer (model 80-365B) and a Mg K_α (1253.6 eV) X-ray source. High-resolution spectra were obtained at 45° take-off-angle by a concentric hemispherical analyzer, operating in the constant pass energy mode at 29.35 eV, using a 720 μm diameter analysis area. Charge referencing was done against adventitious carbon (C 1s at 284.8 eV). The pressure in the analysis chamber was kept lower than 5·10⁻⁶ Pa. PHI ACCESS ESCA-V6.0 F software package was used for data acquisition and analysis. A Shirley-type background was subtracted from the signals. Recorded spectra were always fitted using Gauss-Lorentz curves in order to determinate more accurately the binding energy of the different element core levels.

Elemental analysis (C, H, N and S) was performed by using a LECO analyzer, CHNS-932 model, coupled to a pyrolysis oven LECO VTF. An inductively coupled plasma emission and mass spectrometry Perkin Elmer Optima 7300 DV, with a nebulizer gas flow of 0.6 L/min, a plasma gas flow of 15 L/min and potential RF ICP 1300W, were used for elemental analysis of liquid solutions.

2.3. Catalytic reaction

Catalytic experiments were performed in batch, by using a glass pressure tube with thread bushing (Ace, 15 mL, pressure rated to 10 bars) and magnetic stirring. In a typical procedure, 2 g of D-sorbitol (SigmaUltra, >99%) and 0.100 g of catalyst were loaded into the reactor. Prior the experiments, reactors were always purged with nitrogen. The reaction mixture was heated with a thermostatically controlled oil bath and magnetically stirred at 600 rpm. After reaction time, the reaction was quenched by submerging the reactor in a water bath cooled with ice. Remaining sorbitol and reaction products were separated from the solid resin by adding distilled water. Liquid phase was filtered and the analysis of products was performed by high performance liquid chromatography (HPLC). A JASCO instrument, equipped with quaternary gradient pump (PU-2089), multiwavelength detector (MD-2015), refractive index detector (RI-2031-PLUS), autosampler (AS-2055), column oven (CO-2065) and a Monosaccharide Phenomenex REZEX Ca²⁺ Monosaccharide (300 mm × 7.8 mm) column for sugars detection, was employed. The remaining sorbitol and reaction products were monitored using the refractive index detector. The column is set at 80 °C and distilled water was used as mobile phase (flow rate 0.6 mL/min).

3. Results and discussion

The main physico-chemical characteristics of resins are compiled in Table 1. They possess large pore diameters which provide easy accessibility to sulfonic acid sites, thus preventing diffusional limitations. Two types of commercial resins have been used: i) macroreticular structures, with low (A-70) and high (A-35, P-CT275, P-CT269) crosslinking degree, and ii) gel-type resins (P-PD206) with non-permanent porosity, unlike macroreticular resins whose high crosslinking degree maintains a permanent porosity, with suitable textural properties. Concerning the sulfonation degree, A-70 is conventionally sulfonated, whereas the rest of resins are oversulfonated, as can be inferred from their high acid capacity (Table 2).

Chemical analysis (C and S) of Purolites has confirmed their different degree of sulfonation, as could be inferred from the S/C molar ratio (Table 2). The acid capacity has been deduced from the percentage of sulphur, and values differ from those provided by the supplier. However, the highest value is obtained for P-CT275, according to the acid capacity values provided by the supplier, but,

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