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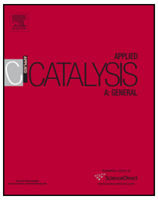

Feature Article

Dehydration of sorbitol to isosorbide in melted phase with propyl-sulfonic functionalized SBA-15: Influence of catalyst hydrophobization

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ABSTRACT

Propyl sulfonic acid functionalized mesostructured SBA-15 silicas have been used to promote the dehydration of sorbitol to isosorbide, in melted phase, under atmospheric pressure. These materials were prepared with different acid capacities and modified with different types of methylsilane functionalities, looking for an enhancement of the catalytic activity of these solid acids in the studied reaction. These two strategies seemed not only to condition the way in which reactants interact with the surface and the catalytic acid sites, i.e. through variations in the hydrophilic/hydrophobic balance, but a change in the acid strength of the catalytic sites is also influenced. Results indicate that increasing the acid loading slowed down the first reaction stage (sorbitol to sorbitan) but boosted the second one (sorbitan to isosorbide), because the interaction of the same sorbitol molecule with more than one acid site difficult its conversion, but increase acid strength, favoring the second dehydration step. Similarly, the organic modification of the solid acid SBA-15-based materials with hydrophobic methylsilane functionalities moieties reduced the affinity of the sorbitol substrate for the catalyst surface, but it also enhanced acid strength as well as the accesibility of sulfonic acids, slowing down the first step, but enhancing the second one. Despite of the influence of both assayed strategies on the catalytic performance of the tested materials is opposite in both dehydration steps, the positive influence of the same on the second reaction stage was proved to be dominant, because of being the limiting step on the conversion of sorbitol to isosorbide. In this way, using highly acid loaded sulfonic acid functionalized SBA-15 modified with surface grafted methylsilanes can be considered the right combination to maximize isosorbide production using these catalysts.

1. Introduction

Sorbitol is a sugar alcohol, currently derived from hydrolysed starch, which can be easily obtained via hydrogenolysis of glucose. Sorbitol is an important platform molecule used as a starting point in the synthesis of a large variety of chemicals [1]. One of these routes is the dehydration of sorbitol to produce anhydrosugar alcohols, such as mono-anhydrosorbitol and di-anhydrosorbitol. Sorbitan, a food additive, and isosorbide, an organic diol, are good examples of sorbitol-derived alcohols. Both products have multiple commercial applications and they can be used to synthesize numerous final products and chemical intermediates such as surfactants, polymers, drugs and cosmetics [2,3].

Isosorbide is conventionally obtained by sequential dehydration of sorbitol to sorbitan, and from this to isosorbide (Scheme 1). This transformation requires the presence of strong acids such as sulfuric or hydrochloric acid as catalysts [4–6], but the use of such mineral acids involves several drawbacks such as a difficult separation of isosorbide from the reaction mixture, or equipment corrosion, as far as the environment and safety are concerned. Therefore, several heterogeneous alternatives have been addressed, including zeolites in acid form [7–9], cation exchange resins [10–12], sulfonated carbons [13], or sulfated metal oxides [14–17], among many others [19,20]. All these studies are focused on developing a heterogeneous catalytic system suitable for sorbitol conversion, but most of them require applying severe reaction conditions -high temperatures, low pressures, and long reaction times-, thus compensating the lack of enough catalytic activity to provide satisfactory isosorbide yields. Therefore, the development of an efficient solid acid catalyst capable to operate under milder

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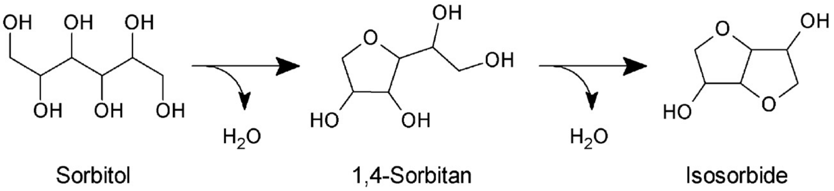

Scheme 1. Dehydration of sorbitol to isosorbide.

reaction conditions, while providing suitable product yields, is still a challenging task.

Recent studies have disclosed that the strength and nature of the acid sites play an important role both on the extent of sorbitol conversion as well as on its selective transformation to isosorbide. It has been stated that sulfonic acid moieties, such as those present in methyl- or *p*-toluene sulfonic acids, provide strong Brønsted acidity with satisfactory catalytic activity in the transformation of sorbitol to isosorbide at mild temperatures [21]. This has prompted several authors to study the catalytic activity of these functionalities when immobilized onto solid supports like silica [22,23], finding a very high catalytic activity in these materials. Despite the nature of the catalytic acid sites is one of the main variables influencing the activity of catalytic systems, it is not the only one. Thus, some authors have brought the attention to a different point with a crucial influence on the dehydration of sorbitol over heterogeneous catalysts: the hydrophobicity of the catalyst surface. Obviously, dehydration reactions necessarily involve the formation of water as by-product, and thus, the hydrophilicity/hydrophobicity of the heterogeneous catalysts play an important role in this type of reactions, conditioning the retention or repulsion of not only the evolving water molecules, but also the reaction substrate and products. This phenomena has been described in the case of high silica aluminosilicate zeolites [8,9], and sulfonated polymers [24,25].

Within the scope of this work, we present the study on the catalytic behavior of mesostructured SBA-15 silica functionalized with propyl sulfonic acid groups and conveniently hydrophobized by means of post-synthetic surface silylation procedures. The combination of different loadings of highly active sulfonic acid species with different surface hydrophobization degrees has been studied in sorbitol dehydration to isosorbide.

2. Experimental

2.1. Materials

D-sorbitol (Sigma-Aldrich) was used as feedstock without previous purification in dehydration tests. Tetraethylorthosilicate (TEOS, 98%, Aldrich) was used as silica precursor in the synthesis of the silica-based mesostructured materials, whereas (3-mercaptopropyl) trimethoxysilane (MCPTMS, Aldrich) was used as sulfonic acid groups precursors in the synthesis of the acid catalysts. Trimethyl chlorosilane (TMCS, Aldrich), dimethyl dichlorosilane (DMDCS, Aldrich) and methyl trichlorosilane (MTCS, Aldrich) were used as silanization agents through a post-synthesis grafting method for the hydrophobization of sulfonic SBA-15 materials. Pluronic triblock copolymer P123 (Aldrich) was used as SBA-15 structure template, and hydrogen peroxide (30% wt, aldrich) as oxidant for the transformation of thiol functionalities into sulfonic acid groups.

2.2. Catalysts synthesis

Propyl-SO_3H SBA-15 (SBA-15-Pr-SO_3H) functionalized with 5, 10 and 15 mol% of propyl sulfonic acid groups (percentage of Si atoms linked by Si—C bond to propyl sulfonic moieties to the total number of Si atoms present in the synthesis medium). Propyl sulfonic acid-functionalized SBA-15 materials were synthesized following the procedure described by Margolese *et al.* [26]. In a typical synthesis batch, 4 g of P123 were dissolved in 125 mL of a 1.9N hydrochloric acid aqueous solution at rt. The clear solution was then warmed up to 40 °C before adding the TEOS. The resultant white suspension was stirred for 45 min before the addition of (3-mercaptopropyl)trimethoxy silane, together with an excess of the hydrogen peroxide used as oxidant. The mixture was then stirred for 20 h, and hydrothermally aged at 110 °C under static conditions in an autoclave for 24 additional hours. The material was then filtered and air dried overnight. The surfactant was removed by ethanol washing under reflux for 24 h (1.5 g of as-made material per 400 mL of ethanol).

2.3. Post-synthesis grafting procedure

Surface modification was accomplished by end-capping the free surface silanol groups with an alkyl-based silane. Typically, 2 g of previously dried 10 mol% sulfonic acid-functionalized SBA-15 was suspended in dry toluene (100 mL). To the resultant suspension, 3 mL of the silylation agent (TMCS, DMDCS, or MTCS) were added, aiming to get different hydrophobization degrees in the final materials, and the resultant suspension was refluxed for 12 h. The solids were recovered by filtration and dried in a vacuum oven at 120 °C overnight.

2.4. Characterization techniques

The textural properties of the catalysts were assessed through N_2 adsorption-desorption experiments performed in a Micromeritics TriStar 3000 unit. Surface area values were calculated from isotherm data using the B.E.T. method. Pore sizes distributions were calculated through the B.J.H. method using the K.J.S. correction. Total pore volume was assumed to be that recorded at $p/p_0 = 0.985$. Structural ordering was further assessed by means of X-ray powder diffraction, performed on a Philips X'Pert diffractometer using the CuKα radiation line in the 2θ angle range of 0.6–5° with a resolution of 0.02°. The amount of silica-supported sulfonic acid groups was calculated by means of elemental analysis to assess the sulfur content using an Elementar Vario EL III unit. Acid capacities were potentiometrically determined using 2 M NaCl (aq) as cationic-exchange agent, and a dropwise addition of 0.01 NaOH (aq) as titration agent. Single-pulse solid-state ^{29}Si MAS-NMR spectroscopy was used to characterize the environment of the silicon nuclei. NMR experiments were conducted at room temperature at a magnetic field strength of 9.4 T on a high-resolution Varian Infinity Plus 400 NMR spectrometer operating at a frequency of 79.41 MHz. Chemical shifts were referenced to tetramethylsilane, and the spectra were recorded using a 3.5 μs π/2 pulse, a recycle delay of 60 s, and 1000 transients. TG analyses were performed using a simultaneous DSC-TGA SDT 2960 thermogravimetric scale. Prior to their analysis, samples were equilibrated in a 50% relative humidity atmosphere at 75 °C for over 100 h. Sorbitol adsorption isotherms were obtained by mixing 0.05 g of solid acid with 10 mL of methanolic solutions of sorbitol and isosorbide, using an

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