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Screening of mono- and bi-functional catalysts for the one-pot conversion of cellobiose into sorbitol

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ABSTRACT

With the ultimate goal of producing robust catalysts for the one-pot conversion of cellulose to sorbitol, a number of solid acids were first investigated for the hydrolysis of cellobiose (model compound). In particular, acid functionalization, catalyst recyclability and hydrothermal stability were evaluated for SBA-15. In the second part of the work, the impregnation of Ru nanoparticles (RuNPs) on the Amberlyst 15 (A15) for the preparation of the bi-functional catalyst 3% RuNPs/A15 for the one-pot conversion of cellobiose into sorbitol is described. The performances of the bi-functional catalyst, 5% Ru/C and the physical mixture of the 5% Ru/C and A15 were evaluated for the conversion of cellobiose to sorbitol. When the bi-functional catalyst was employed, 81% yield of sorbitol was obtained after 5 h of reaction. In contrast, the best result with the physical mixture gave less than 53% yield of sorbitol after 5 h, indicating that the bi-functionality of the 3% RuNPs/Amberlyst 15 catalyst plays a major role in this reaction.

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1. Introduction

The uncertainty regarding the future supply of oil, the increasing energy demands per capita and the need for reducing the environmental impact of processes and products has been the driving force behind the development of a new industry based on renewables. In this present scenario, the efficient use of lignocellulosic biomass and its conversion in high value products has become one of biggest challenges for both the academia and industry [1].

In the past ten years, a lot of work has been done in optimizing conditions for hydrothermal hydrolysis of both cellulose and hemicellulose [2–4]. However, even with these optimized conditions a broad distribution of by-products is obtained. On the other hand, the hydrogenation of sugars is already a well-established industrial process, but the severe reaction conditions along with the possibility of producing sugar alcohols from different feedstocks undoubtedly offer room for improvement. In this context, the one-pot conversion of polysaccharides into sugar alcohols is a

very interesting route as the sugar monomers (glucose and xylose) are hydrogenated to more stable products (e.g. sorbitol & xylitol), producing higher value products and minimizing the formation of by-products in the hydrolysis step [5,6].

Most of the literature on the topic describes the one pot conversion of polysaccharides into sugar alcohols. The catalysts employed in these studies can be classified in two groups: metallic and bifunctional catalysts. Within the metallic group, the most used catalysts are the ruthenium based ones [5–9] due to their ability to promote both hydrogenolysis and hydrogenation. In these systems, the polysaccharide is believed to be broken into sugars by hydrolysis (catalyzed or not) and by hydrogenolysis catalyzed by the Ru catalysts. When aiming to produce sugar alcohols such as sorbitol and xylitol using metal catalysts one of the challenges is to avoid further hydrogenolysis of the products [10–14]. Bi-functional catalysts can provide both acid sites and metallic sites [15–20]. The acid sites promote the hydrolysis whereas the metallic sites mostly promote sugar hydrogenation. Such catalysts typically comprise a solid acid support decorated with metallic sites.

It is well known that in the coupled hydrolysis-hydrogenation of polysaccharides the hydrolysis is usually the rate determining step [5,21,22]. Therefore, the choice of the solid acid for the preparation of a bi-functional catalyst is very important. Ideally, the solid acid

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should not only be able to catalyze the hydrolysis of the substrate but also ought to be very stable under reaction conditions; otherwise, the leaching of the acid sites would result in a decrease of activity in the hydrolysis [10,20,23–26]. Furthermore, the leaching of the acid sites can increase the rate of the metal leaching which is further detrimental.

In the present work, a series of solid acids has been screened for cellobiose hydrolysis. The performance of these materials was evaluated in terms of glucose yield, catalyst stability and recyclability. In the second part of the work, A15 is impregnated with pre-formed ruthenium nanoparticles, to form the bi-functional catalyst: 3% RuNPs/A15. After that, the performances of this bi-functional catalyst, a catalyst 5% Ru/C and the physical mixture (5% Ru/C + A15) were compared for the one pot conversion of cellobiose to sorbitol, highlighting and discussing the superior results obtained with this bi-functional catalyst.

2. Experimental

2.1. Materials

Tetraethyl-orthosilicate (TEOS), 3-mercaptopropyltrimethoxysilane (3-MPTMS), cellobiose, 5-hydroxymethyl furfural (HMF), glucose, Amberlyst-15 (A15), D-(+)-cellobiose, ruthenium on carbon (5% Ru/C), ruthenium (III) chloride hydrate, acetone (HPLC grade), ethylene glycol anhydrous and polyvinylpyrrolidone (PVP) 10,000 MW were purchased from Sigma Aldrich and used without further purification.

Analytical grade reagents hydrochloric acid (HCl 37% w/w), hydrogen peroxide (H₂O₂ 30% w/w), sulfuric acid (H₂SO₄ 96% w/w), phosphoric acid (H₃PO₄ 85% w/w) were purchased and used without further purification.

2.2. Catalyst preparation

2.2.1. Bi-functional catalyst preparation

The 3% RuNPs/A15 catalyst was prepared according to the following procedure: PVP stabilized ruthenium nanoparticles were synthesized using a procedure adapted from the work of Yan et al. [27]. Typically, RuCl₃·nH₂O (0.0371 g, 1.5 × 10⁻⁴ mol) and PVP (MW = 10000, 0.1667 g, 1.5 × 10⁻³ mol) were dissolved in ethylene glycol (150 ml) giving a dark red solution. This solution was then heated to reflux (198 °C) with vigorous stirring. After 3 h, a dark brown colloidal solution containing the RuNPs was obtained. To the solution, 750 ml of acetone were added and left to stir for 12 h. The RuNPs were recovered by centrifugation and re-dispersed in water. Finally, RuNPs were impregnated to A15 by wetness impregnation using a w/v (g/ml) ratio of 10.

2.2.2. SBA-15 Synthesis

The protocol used in this study was adapted from Meynen et al. [28], a solution of concentrated HCl 37% w/w (20 ml) and H₂O (130 ml) was prepared and 4 g of P123 was added and the solution was left to stir until complete dissolution of the templating agent. Subsequently, TEOS (9.14 ml) was added to the P123 acid solution and the mixture was left to stir for 7.5 h at 45 °C. The formed mesoporous material was left aging for 15.5 h at 80 °C under static conditions. At the end of the aging step, the mixture was cooled down to room temperature, and the white solid precipitate was filtered and washed 3 times with distilled water and dried at room temperature overnight. The templating agent was removed by calcination by treating the material at 550 °C.

2.2.3. Sulfonic acid functionalized SBA-15 via post surface grafting

SBA-15 was then functionalized with propyl-sulfonic acid groups following the protocol reported by Siril et al. [29]. SBA-15-SO₃H catalysts was prepared with S/Si ratio of 0.30 (SBA-15-S-0.3). Typically, SBA-15 (1.5 g) was suspended in toluene (15 ml) and refluxed for one hour at 115 °C under stirring. Subsequently, the appropriate amount of 3-MPTMS was added to the suspended solid and the mixture was kept at 115 °C for 24 h under stirring. The mixture was then left to cool down to room temperature and the recovered solid was filtered, washed 3 times with distilled water and dried overnight at room temperature. The dry solid was then suspended in 30% w/w H₂O₂ solution and left under stirring for 1 h in a closed vessel. The recovered solid was then filtered, washed with water and left to dry overnight at room temperature. Finally, SBA-15 acid treated with a 10% v/v H₂SO₄ solution for 1 h under stirring, and then filtered, washed 3 times with distilled water and left to dry at room temperature overnight.

2.2.4. Phosphoric acid functionalized SBA-15 via post surface grafting

The phosphoric acid functionalized catalyst was synthesized according to the method reported by Wu et al. [30]. Typically, SBA-15 (1 g) was suspended in acetone (40 ml) and the appropriate amount of H₃PO₄ (85% w/w) was added. The suspended catalyst was stirred at room temperature for 6 h. The solvent was removed with a rotary evaporator at 60 °C, and the recovered solid calcined at 500 °C (4 h). Subsequently, the material was left to cool down. The materials were denoted SBA-15-P-X where X states for the P/Si molar ratio values used for the preparation, namely: 0.15, 0.3, 0.6.

2.3. Characterization

TEM characterization was performed on the supported 3% RuNPs/A15 catalyst using a JEOL JEM 2100 LaB₆ instrument at 200 kV accelerating voltage. Catalysts were sonicated in methanol and supported on holey carbon film on copper grids (300 mesh). Particle size distributions were determined from 300 particles.

Powder X-ray diffraction patterns (PXRD) were recorded in transmission mode with a PANalytical X'Pert Pro HTS diffractometer with a slit of 0.04° from 0.5 to 70° 2θ using a Cu Kα radiation.

UV-vis spectroscopy was used to monitor the synthesis of the PVP stabilized ruthenium nanoparticles using the Thermo Scientific evolution 260 spectrophotometer. The Brønsted-acidity of the catalysts was determined by titration method described elsewhere [31] using the Mettler Toledo G20 Compact Titrator. The surface area and pore volume values of A15 and 3% RuNPs/A15 were measured by N₂ BET analysis on a Micromeritics ASAP 2420 and the samples were degassed overnight at 90 °C prior to the analysis. The ICP-OES of reaction medium were performed using the instrument ICP-OES-SoP, Spectro Ciros CCD.

2.4. Catalytic testing

In the screening of the solid acids for hydrolysis of cellobiose the reactions were carried out in a 5000 multiple Parr reactor system which consists of 6 vessels of 75 ml. 30 ml of a 30 mmolL⁻¹ cellobiose solution with 25 mg of catalyst was introduced in the vessel. The reactor was heated up to 150 °C with a stirring of 700 rpm for two hours under autogenous pressure.

The one-pot conversion of cellobiose into sorbitol experiments were carried out in a 50 ml Parr reactor. The reaction mixture was added to the vessel then the reactor was flushed three times with nitrogen before being heated up to the desired temperature. When the correct temperature was reached hydrogen gas was charged

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