Direct catalytic production of sorbitol from waste cellulosic materials

Lucília Sousa Ribeiro, José J. de Melo Órfão, Manuel Fernando Ribeiro Pereira *

Laboratório de Processos de Separação e Reação-Laboratório de Catálise e Materiais (LSRE-LCM), Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

HIGHLIGHTS

- Materials ball-milling disrupted their crystallinity, easing the direct conversion.
- Sorbitol was directly obtained from cotton wool, cotton textile and tissue paper.
- Mix-milling greatly enhanced the rate of conversion of cellulosic biomass.
- Sorbitol amounts higher than 0.5 g could be obtained from 1 g of cellulosic biomass.
- Printing paper (white and recycled) was not converted to sugar alcohols.

GRAPHICAL ABSTRACT
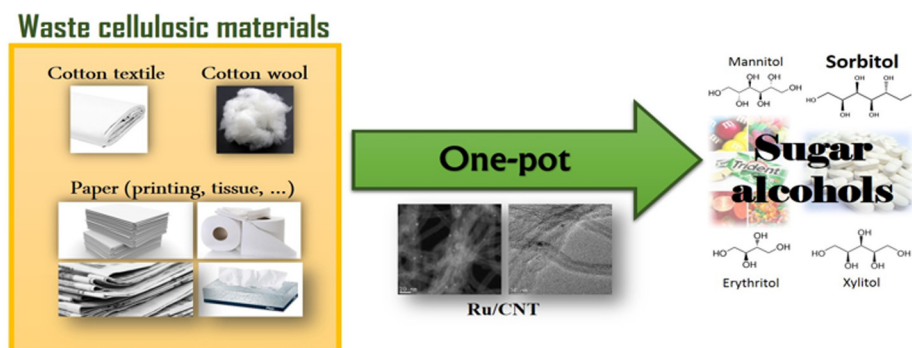
ABSTRACT

Cotton wool, cotton textile, tissue paper and printing paper, all potential waste cellulosic materials, were directly converted to sorbitol using a Ru/CNT catalyst in the presence of H_2 and using only water as solvent, without any acids. Conversions up to 38% were attained for the raw substrates, with sorbitol yields below 10%. Ball-milling of the materials disrupted their crystallinity, allowing reaching 100% conversion of cotton wool, cotton textile and tissue paper after 4 h, with sorbitol yields around 50%. Mix-milling these materials with the catalyst greatly enhanced their conversion rate, and the materials were efficiently converted to sorbitol with a yield around 50% in 2 h. However, ball- and mix-milled printing paper presented a conversion of only 50% after 5 h, with sorbitol yields of 7%. Amounts of sorbitol of 0.525, 0.511 and 0.559 g could be obtained from 1 g of cotton wool, cotton textile and tissue paper, respectively.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Concerns about global warming have motivated the search for alternative renewable resources, leading to a significant increase in research activities directed towards their use (Byun and Han, 2016a,b; Deng et al., 2015; Kobayashi et al., 2014). Currently, about 10% of the world's primary energy is biomass, which is mostly used to generate power and heat (Li et al., 2015). Lignocellulose is the most abundant and less expensive type of biomass on earth, therefore being a promising feedstock for the production of renewable energy, especially biofuels, and chemicals (Deng et al., 2015; Feng et al., 2016). Unlike corn and stalk, lignocellulose is inedible for humans, and its use will not impose a negative impact on food supplies since it does not compete with food production (Li et al., 2015; Yamaguchi et al., 2016). Lignocellulose consists of 35–50% cellulose (a polymer of D-glucose), 25–30% hemicellulose (a polymer of

C_5 and C_6 sugars) and 15–30% lignin (Deng et al., 2015). The hydrolytic hydrogenation of these sugar polymers produces sugar alcohols, which are used as low-calorie and low-cariogenic sweeteners and sugar substitutes for diabetics, as humectants in cosmetic and pharmaceutical products, in paper and tobacco and as precursors to plastics (Kobayashi et al., 2014; Kusserow et al., 2003; Mäki-Arvela et al., 2011; Rao et al., 2016). Sorbitol is one of the most important sugar alcohols and can serve as platform chemical for the synthesis of various value-added chemicals such as glycerol, glycols, lactic acid, isosorbide, 1,4-sorbitan and ʟ-sorbose (Deng et al., 2015). The annual production of sorbitol has already reached 6.5×10^5 ton (Kobayashi et al., 2014). Therefore, the catalytic hydrolytic hydrogenation of biomass and its components in the presence of hydrogen has greatly attracted attention for the establishment of a sustainable society, because it circumvents metastable glucose and allows high selectivity to high-value chemicals or fuels (Zhao et al., 2015).

The catalytic conversion of cellulose to sorbitol using supported metal catalysts in the presence of hydrogen has already been reported by some research groups (Deng et al., 2009; Ding et al., 2010; Fukuoka and Dhepe, 2006; Kobayashi et al., 2011; Luo et al., 2007; Ribeiro et al., 2015b; Romero et al., 2016; Van de Vyver et al., 2010, 2012; Yang et al., 2012). Carbon nanotubes, which have been gaining increasing attention as supports in heterogeneous catalysis, have already shown to be the most effective support for the direct conversion of cellulose to sorbitol (Deng et al., 2009; Ribeiro et al., 2017; Wang et al., 2012). Also, Ru catalysts have shown to be the most effective in the direct conversion of cellulose into polyols (Deng et al., 2009; Guo et al., 2014; Ribeiro et al., 2015a; Wu et al., 2012). However, pure cellulose has to be obtained from lignocellulose, normally using strong acid/base catalysts to completely remove the hemicellulose and lignin components. Thus, the direct conversion of the individual components in woody biomass to valuable chemicals is of great importance to open new possibilities of using biomass (Yamaguchi et al., 2014). Palkovits et al. reported the conversion of spruce chips using supported metal catalysts combined with sulfuric/phosphoric acid with a yield of 55% (based on cellulose) of sugar alcohols (sorbitol, sorbitan, isosorbide) (Palkovits et al., 2010). However, the use of acids has problems associated with corrosion of the reactor or neutralization processes for the removal of the acid, and so should be avoided. Beeck et al. also studied the conversion of several lignocellulosic biomass into sorbitan and isosorbide (yield of 15% based on carbon) using a combination of supported Ru catalyst and heteropoly acids (Beeck et al., 2013). Nevertheless, the acid catalysts were still required so far for the conversion of lignocellulosic materials to sugar alcohols. Guha et al. were successful in producing arabitol from sugar beet fiber (yield of 83% based on hemicellulose) (Guha et al., 2011), but the direct catalytic conversion of cellulose in lignocellulosic biomass remained a challenge. Recently, Yamaguchi et al. directly converted cellulose and hemicellulose in wood chips using 4%Pt/BP2000 in water without the use of any acids, achieving a 94% conversion and 62% yield of sugar alcohols (Yamaguchi et al., 2014). Using tungsten-based catalysts, Li et al. managed to convert raw woody biomass (poplar, basswood, ashtree, beech, xylosma, bagasse, pine and yate) into ethylene glycol and other diols with a total yield up to 75.6% (based on the amount of cellulose and hemicellulose) and into monophenols with a yield of 46.5% (based on lignin) (Li et al., 2015). More recently, Yamaguchi et al. also reported the direct conversion of lignocellulosic biomass (Japanese cedar, eucalyptus, bagasse, empty fruit bunch and rice straw) into sugar alcohols (sorbitol, mannitol, galactitol, xylitol, arabitol) using supported Pt and Ru-Pt catalysts in the presence of hydrogen in water without any acids, obtaining an amount of sugar alcohols up to 0.551 g from 1 g of milled bagasse (Yamaguchi et al., 2016).

Although these works have already focused on the conversion of woody biomass, such as forestry wastes, agricultural residues and crops, to the best of our knowledge the direct conversion of materials that are mainly composed of cellulose and also considered as residues, such as paper or cotton, has not yet been reported. So, this work will focus on the one-pot catalytic conversion of waste cellulosic materials into high added-value chemicals, especially sorbitol, in the presence of a Ru catalyst supported on multi-walled carbon nanotubes, using only water as solvent under H_2 pressure. The performance of the metal catalyst will be examined in the conversion of cellulosic materials that are normally considered as residues, such as printing paper (white or recycled), tissue paper, cotton wool and cotton textile. Furthermore, the process used in this work can be considered environmentally friendly, since only uses water as solvent and does not require the use of any acids for the reaction neither for the pre-treatment of the substrates or catalyst. Additionally, the effect of ball-milling the substrates or mix-milling them with the catalyst will also be considered.

2. Materials and methods

2.1. Materials

A cotton textile sample was supplied by Arcotêxteis (Portugal), with the following features: 100% cotton prepared for dyeing (warp: 3726 threads, weft: 52 threads), previously desized and bleached. Cotton wool (Continente), printing paper (Navigator Universal, 80 g·m^2) and tissue paper (Renova) were acquired from Continente and recycled printing paper (Staples 100% recycled, 80 g·m^2) from Staples. Microcrystalline cellulose, sorbitol (98%) and the metal precursor ruthenium (III) chloride ($RuCl_3$ 99.9%, Ru 38%) were provided by Alfa Aesar. Nanocyl-3100 multi-walled carbon nanotubes were obtained from Nanocyl and sulphuric acid (>95%) was supplied by Fisher Chemical. TiO_2 P25 was obtained from Degussa. Ultrapure water with a conductivity of 18.2 μS·cm^{-1} was obtained in a Milli-Q Millipore System and used for the preparation of the solutions.

2.2. Preparation procedures

The different materials were ball-milled in a 10 cm^3 ceramic pot with two zirconium oxide balls (12 mm of diameter) using a laboratory ball mill (Retsch Mixer Mill MM200) for 4 h at a frequency of 20 vibrations/s.

The different materials were also ball-milled together with the catalyst in the same conditions, by introducing both catalyst and substrate in the same ceramic pot.

A 0.4 wt% ruthenium catalyst was prepared by the incipient wetness impregnation of commercial multi-walled carbon nanotubes (CNT) with an aqueous solution of the metallic precursor ($RuCl_3$). This metal loading has shown to be an optimum for the transformation of cellulose into sorbitol under the present conditions (Ribeiro et al., 2015a). After impregnation, the resulting material was dried overnight in an oven at 110 °C. Finally, the catalyst was heat treated under nitrogen flow for 3 h at 250 °C and subsequently reduced under hydrogen flow for 3 h at 250 °C. The sample was denoted as Ru/CNT.

Further details can be found elsewhere (Ribeiro et al., 2017).

2.3. Characterization

X-ray diffraction (XRD) patterns were recorded by a Phillips X'Pert MPD diffractometer (Cu-Kα = 0.15406 nm), where the diffracted intensity of Cu-Kα radiation was measured in the