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Direct conversion of cellulose to sorbitol over ruthenium catalysts: Influence of the support

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ABSTRACT

Ruthenium-based catalysts were prepared by incipient wetness impregnation of different supports and characterized by TPR, TEM, ICP and N₂ adsorption at –196 °C. The catalytic performances of the catalysts were evaluated in the hydrolytic hydrogenation of cellulose. The prepared catalysts were highly efficient, allowing conversions of cellulose higher than 75% after 5 h of reaction. The highest selectivity to sorbitol (over 60%) was reached when using carbon nanotubes (CNT) as support. Moreover, if this catalyst was ball-milled together with cellulose, that selectivity to sorbitol could be achieved in only 1 h of reaction and with complete conversion of cellulose.

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1. Introduction

Currently, much attention is being paid to the foreseeable dwindling of fossil fuel supplies and the resultant energy crisis, as well as the urgent need to control the emission of green-house gases [1]. Being the only renewable carbon source on earth, biomass has the potential to serve as a sustainable source for both energy and organic carbon [2,3]. Many efforts have been made by different research groups in the valorisation of lignocellulosic biomass, as is the case of the hydrolytic hydrogenation of cellulose [4–11]. The hydrolytic hydrogenation of cellulose is highly desired since it circumvents metastable glucose allowing the high selective formation of high-added value chemicals in just one-step using water at high temperatures and in the presence of hydrogen [12]. This process generally involves two steps – the hydrolysis of cellulose to glu-

cose, promoted by acid sites, followed by its hydrogenation into sugars and sugar alcohols. Sorbitol is classified as one of the ten versatile bio-based platform molecules having significant applications in foods, pharmaceuticals and cosmetics [13,14], and also as raw material for the synthesis of many other fine chemicals such as L-ascorbic acid (vitamin C), isosorbide [15], 1,4-sorbitan, glycols, glycerol and lactic acid [5,16,17].

Heterogeneous catalysis allows the development of environmentally friendly processes that lead to selective formation of value-added products from cellulose [18]. Solid catalysts are also expected to be favourable for the conversion of cellulose due to their ease of separation from the reaction mixture, reusability and applicability for various reaction conditions [19]. Ruthenium catalysts have shown to be the most effective in the direct conversion of cellulose into sugar alcohols [10,20]. Carbon materials such as activated carbon and carbon nanotubes are known as heat- and water-tolerant supports, reason why carbon supported metal catalysts have been extensively studied [10,12,21]. Activated carbon is most often used to stabilize Ru particles and is cheap, while carbon nanotubes are promising supports, but are more expensive. As so, the selection of support is also important beyond the active metal selection and parametric optimization for selective production of sorbitol directly from cellulose. It has been observed that Ru loaded on different supports such as activated carbon [21,22], Al₂O₃ [21–23], TiO₂ [22,24], carbon nanotubes [10] and carbon

Abbreviations: AC, activated carbon; CNT, carbon nanotubes; EG, ethylene glycol; GEN, graphene; GIT, graphite; HPLC, high performance liquid chromatography; HY, zeolite HY; ICP-OES, inductively coupled plasma optical emission spectrometry; P80, carbon black P80; PG, propylene glycol; RI, refractive index; TEM, transmission electron microscopy; TOC, total organic carbon; TOF, turnover frequency; TPR, temperature programmed reduction; XG, carbon xerogel.

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nanofibers [21] have different catalytic performances [9] and their activity/selectivity depends on the support material. Since this question about optimal support remains, the aim of this work is to develop an efficient catalyst for the one-pot catalytic conversion of cellulose to sorbitol under hydrogen by testing various supported ruthenium catalysts.

2. Materials and methods

2.1. Chemicals and materials

The metal precursor ruthenium (III) chloride (RuCl₃ 99.9%, Ru 38%) and microcrystalline cellulose were supplied by Alfa Aesar. Activated carbon GAC 1240 PLUS, Nanocyl-3100 multi-walled carbon nanotubes, graphene, carbon black (Printex 80) and alumina were provided by Norit, Nanocyl, Graphene Technologies, Orion and Buehler, respectively. Graphite and Linde LZ-Y62 zeolite were purchased from Aldrich. Sulphuric acid was obtained from VWR. All solutions were prepared in ultrapure water obtained in a Milli-Q Millipore System.

2.2. Preparation of materials

HY zeolite was prepared by treating the commercial zeolite (Linde LZ-Y62) under air flow for 8 h at 500 °C. Carbon xerogel (XG) was prepared according to the procedure reported elsewhere by Rocha et al. [25].

Different materials were used as supports: activated carbon (AC), carbon nanotubes (CNT), graphite (GIT), graphene (GEN), carbon black P80 (P80), carbon xerogel (XG), alumina (Al₂O₃) and zeolite (HY). The Ru catalysts, with a nominal metal content of 0.4 wt%, were prepared by incipient wetness impregnation of the supports with a solution of the metallic precursor (RuCl₃). Each support was firstly introduced in an ultrasonic bath and, after 30 min, the precursor solution was added dropwise until all the support was wet. Still in the ultrasonic bath, the maturation and drying occurred for 90 min, after which the samples were dried overnight in an oven at 110 °C and then stored for posterior use. After heat treatment under N₂ flow for 3 h at 250 °C, the catalysts were reduced under H₂ flow for 3 h at 250 °C. The appropriate reduction temperature (250 °C) was determined by temperature programmed reduction (TPR) (see Section 3.1). The different catalysts were denominated as Ru/AC, Ru/CNT, Ru/GIT, Ru/GEN, Ru/P80, Ru/XG, Ru/Al₂O₃ and Ru/HY.

Microcrystalline cellulose was ball-milled using a laboratory ball-mill (Retsch Mixer Mill MM200), operating at a frequency of 20 Hz for 4 h (see details in Ribeiro et al. [26]).

2.3. Characterization of materials

The surface areas and pore volumes of supports and catalysts were determined from N₂ adsorption isotherms measured at –196 °C in a NOVA Quantachrome Instruments apparatus. TPR profiles were obtained by a fully automated AMI-200 equipment (Altamira Instruments); the samples were submitted to a 5 °C min⁻¹ heating to 700 °C under 5% (v/v) H₂ flow diluted in He (total flow rate = 30 cm³ min⁻¹). The metal loading of the catalyst was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES). The surface morphology and Ru particle size of the different catalysts were analysed by TEM (JEOL2010F instrument, with 0.19 nm spatial resolution at Scherzer defocus conditions). High Angel Annular Dark Field-Scanning Transmission Electron Microscopy (HAADF-STEM) images were obtained with the same microscope. An electron probe with diameter of 0.5 nm at a diffraction camera length of 10 cm was used for the HAADF mode. Size distributions were determined by the measurement

Table 1
Textural properties of the different supports and Ru/CNT catalyst.

Sample	S _{BET} ^a (m ² g ⁻¹)	S _{meso} ^b (m ² g ⁻¹)	V _{micro} ^b (cm ³ g ⁻¹)
AC	847	145	0.301
GIT	12	12	–
GEN	352	352	–
P80	83	83	–
XG	647	265	0.176
HY	406	96	0.132
Al ₂ O ₃	226	226	–
CNT	267	267	–
Ru/CNT	245	245	–

^a Calculated using the Brunauer-Emmett-Teller (BET) equation.

^b Calculated by the t-method.

of 200 nanoparticles and the average diameter was calculated by $d_M = \frac{\sum d_i n_i}{\sum n_i}$, where n_i is the number of particles with diameter d_i .

Further details can be found elsewhere [26].

Catalysts evaluation

The hydrolytic hydrogenation experiments were carried out with hydrogen under 50 bar, at 205 °C. Ball-milled cellulose (750 mg) and catalyst (300 mg) were added to 300 mL of water in a 1000 mL stainless steel reactor (Parr Instruments, USA Mod. 5120) under stirring at 150 rpm. After heating under nitrogen to the desired temperature, the reaction was initiated by switching from inert gas to hydrogen.

The reaction was monitored by taking samples (1 mL) for analysis at regular time intervals. High performance liquid chromatography (HPLC) with an Alltech OA-1000 ion exclusion column and a refractive index (RI) detector was used to detect liquid products. C2–C6 polyols, including ethylene glycol, propylene glycol, glycerol, erythritol, sorbitol, mannitol and glucose were detected. The selectivity (S_i) of each product i at time t was calculated as:

$$S_i = \frac{C_i}{v_i \times C_0 \times X} \quad (1)$$

where C_i is the concentration of the product i (mol L⁻¹), C_0 is the initial concentration of cellulose (mol L⁻¹), X is the conversion of cellulose and v_i corresponds to the moles of i produced per mol of cellulose consumed, according to the stoichiometry.

For determining the conversion of cellulose, TOC data were obtained with a Shimadzu TOC 5000-A and the conversion (X) determined using the equation:

$$X (\%) = \frac{\text{moles of total organic carbon in the resultant liquid}}{\text{moles of carbon in cellulose charged into the reactor}} \times 100 \quad (2)$$

Further details can be found elsewhere [27].

3. Results and discussion

3.1. Characterization of materials

Fig. 1 shows the TPR profiles of Ru catalysts supported on different materials. Ru/CNT, Ru/P80 and Ru/GIT present wide reduction peaks around 200–300 °C. Ru/AC profile shows a wide reduction peak around 100–300 °C, while Ru/GEN and Ru/Al₂O₃ present reduction ranges around 100–220 °C. Also, the reduction ranges of Ru/XG and Ru/HY are around 50–130 °C and 150–250 °C, respectively. The peaks observed at high temperatures can be attributed to the reduction of the carbon materials, since they are also present in the TPR profiles of the corresponding supports (not shown). According to these results, and for comparative purposes, all catalysts were reduced at 250 °C for 3 h to assure effective reduction of the metal.

Table 1 summarizes the textural properties of the supports and Ru/CNT catalyst determined from N₂ adsorption isotherms. The

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