Lucília S. Ribeiro, José J.M. Órfão and Manuel Fernando R. Pereira*

Comparative study of different catalysts for the direct conversion of cellulose to sorbitol

Abstract: The catalytic conversion of lignocellulosic biomass to obtain high added value compounds and fuels is a rapidly developing field. Given the abundance of this renewable raw material and its reduced impact on the food chain, it is an attractive source for obtaining chemicals or fuels in the context of a sustainable economy. In this work, bi-functional catalysts were developed that were capable of performing in a single step the hydrolysis and hydrogenation of cellulose to produce compounds that may be used in the production of fine chemicals or easily converted into fuels (e.g., sorbitol). Different activated carbon (AC) supported metal catalysts were examined for the one-pot hydrolytic hydrogenation of cellulose. Among the prepared catalysts, 0.4% Ru/AC was shown to be the most active and selective for the conversion of cellulose into sorbitol. When microcrystalline cellulose was used, a conversion of 32% was reached after 5 h of reaction, with a selectivity to sorbitol of 30%. Moreover, ball-milled cellulose allowed attaining conversions over 50%, with selectivities to sorbitol of 45%. The results obtained showed that Ru/AC is effective for the hydrolytic hydrogenation of cellulose to sugar alcohols and that the conversion can be greatly improved by using the substrate after pre-treatment by ball-milling.

Keywords: biomass; cellulose; hydrolytic hydrogenation; Ru catalyst; sorbitol.

*Corresponding author: Manuel Fernando R. Pereira, Laboratory of Catalysis and Materials (LCM), Associate Laboratory LSRE-LCM, Faculty of Engineering, Department of Chemical Engineering, University of Porto, Rua Dr. Roberto Frias, s/n 4200-465, Porto, Portugal, e-mail: fpereira@fe.up.pt
Lucília S. Ribeiro and José J.M. Órfão: Laboratory of Catalysis and Materials (LCM), Associate Laboratory LSRE-LCM, Faculty of Engineering, Department of Chemical Engineering, University of Porto, Rua Dr. Roberto Frias, s/n 4200-465, Porto, Portugal
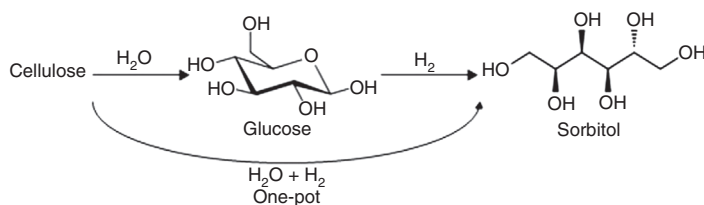
1 Introduction

Concerns about the depletion of fossil fuel reserves, global climate change and increasing energy demands have encouraged the exploration of new renewable alternatives to fossil raw materials for production of energy, fuels and chemicals [1–3]. Cellulose, the most abundant source of biomass on Earth, is currently regarded as a promising alternative for the sustainable supply of fine chemicals and fuel, as it cannot be digested by humans and thus its use, unlike corn or starch, will not impose a negative impact on food supplies [4, 5]. The development of an efficient and sustainable catalytic process for the conversion of cellulose into target products has been regarded as one viable way to reduce CO_2 emissions and alleviate the energy crisis, providing a long-term solution to the industrial dependence on fossil carbon [5]. One of the alternative is the one-pot hydrolytic hydrogenation of cellulose to sugar alcohols over bi-functional heterogeneous catalysts. The reaction involves the hydrolysis of cellulose into glucose followed by the hydrogenation into sugar alcohols (Figure 1). The sugar alcohols produced are non-carcinogenic polyols possessing a reduced calorific value with many applications in the food and pharmaceutical industries [6]. Sorbitol ([2S,3R,4R,5R]-hexane-1,2,3,4,5,6-hexol) is one of the most important intermediates, being widely used as sweetener, dispersing agent and humectant in pharmaceuticals, cosmetics, and textiles, as well as platform chemical for the synthesis of chemical compounds such as isosorbide, sorbitan, glycerol, L-sorbose, vitamin C, etc. [3, 7, 8].

However, although some studies have succeeded in converting cellulose into sorbitol or other high-valued chemicals, the selective production of sorbitol with high yields as well as the valorisation of cellulose are still challenging [7, 9], mostly due to the cellulose's robust crystalline structure and insolubility in conventional solvents. Most processes suffer from high energy consumption and low chemical selectivity. Therefore, designing more efficient catalytic systems for the conversion of cellulose to platform chemicals is highly desirable. For the hydrolysis of cellulose strong mineral acids, such as hydrochloric acid or sulfuric acid, are traditionally used, but they

Figure 1: One-pot catalytic conversion of cellulose into sorbitol.

are corrosive and have to be separated from the reaction mixture [1, 5]. An ideal alternative is to use a heterogeneous catalyst, which is easily separable from the reaction mixture [2, 10]. So, the suitable catalyst should provide acid sites for the hydrolysis and metallic sites for the hydrogenation. Ruthenium (Ru) catalysts have shown to be the most effective in the direct conversion of cellulose into polyols [2, 11, 12]. However, the problem about the optimization of the support remains. Activated carbon (AC) is most often used to stabilize Ru particles and is cheap [13], whereas carbon nanotubes [11, 14] and nanofibers [15] are promising supports, but are more expensive.

Although exciting progress has been made by several groups [7, 11, 16–18], intensive studies are still required for exploring high-performance catalysts. The aim of this work is to develop an efficient process for the one-pot catalytic conversion of cellulose to sorbitol, using different carbon supported metal catalysts under H_2 pressure.

2 Materials and methods

2.1. Chemicals and materials

Unless stated otherwise, chemicals were purchased from commercial sources and used as received, without further purification. The ultrapure water with a conductivity of 18.2 µS cm^{-1} was obtained in a Milli-Q Millipore System. Microcrystalline cellulose and sorbitol (98%) were purchased from Alfa Aesar (Karlsruhe, Germany). The metal precursors ruthenium(III) chloride (RuCl$_3$ 99.9%, Ru 38%), palladium(II) chloride (PdCl$_2$ 99%, Pd min 59.5%), chloroplatinic acid hexahidrate (H$_2$PtCl$_6$·6H$_2$O 99.9%), hexachloroiridic acid hexahidrate (H$_2$IrCl$_6$ 99.9%, Ir 38-42%) and rhodium(III) chloride (RhCl$_3$, Rh 38.5-45.5%) were also supplied by Alfa Aesar (Karlsruhe, Germany). AC GAC 1240 PLUS was provided by Norit (Amersfoort, The Netherlands) and sulfuric acid (95%) was obtained from VWR (Carnaxide, Portugal).

2.2. Cellulose pre-treatment

In order to facilitate the contact with the catalysts, the crystalline structure of cellulose has to be considered. Mechanical and chemical treatments decrease the degree of crystallization of cellulose (crystallinity index – CrI), and this value can be determined by X-ray diffraction (XRD) and ^{13}C nuclear magnetic resonance (NMR). Milling methods such as ball-milling are the typical mechanical techniques for disrupting the crystal structure of cellulose, since cellulose's hydrogen bonds are cleaved [19].

In this work, microcrystalline cellulose was ball-milled in a ceramic pot with two ZrO$_2$ balls, in order to study its effect in the performance of the process. The ball-milled cellulose sample was prepared using a laboratory ball mill (Retsch Mixer Mill MM200) by charging 1.5 g of commercial microcrystalline cellulose into the ceramic pot, operating at a frequency of 10 Hz for 4 h. The *CrI* of cellulose was determined by XRD (see Section 3.1 for details on the method).

2.3. Catalysts preparation

A commercial Norit GAC 1240 AC sample was used as support for this study. Ru-based catalyst was prepared by incipient wetness impregnation of AC with a solution of the corresponding metallic precursor. The amount of noble metal was calculated to achieve a metal loading of 0.4% wt. The support (AC) was firstly introduced in an ultrasonic bath for 30 min. Secondly, the precursor solution was added dropwise, with a peristaltic pump (50 ml h^{-1}), until all the support was wet. Still in the ultrasonic bath, the maturation and drying occurred during 90 min, after which the catalyst was dried overnight in an oven at 110°C and then stored for posterior use.

After heat treatment under nitrogen flow for 3 h (50 cm^3 min^{-1}), the catalyst was reduced under hydrogen flow for 3 h (50 cm^3 min^{-1}). The appropriate reduction temperature (250°C) was determined by temperature programmed reduction (TPR) (see Section 3.1). The treatment under nitrogen flow was carried out at the same temperature used for the reduction. This sample was denoted as 0.4% Ru/AC.

Following this procedure, two series of catalysts were prepared, one with different metal loadings (0.4, 0.8 and 1.2 wt% Ru) and the other with different metals (0.4% Rh/AC, 0.4% Ir/AC, 0.4% Pt/AC and 0.4% Pd/AC).

2.4. Characterisation of materials

Both support and catalysts were characterized by N$_2$ adsorption isotherms at -196°C and TPR. The nitrogen adsorption isotherms (-196°C) were obtained using a Quantachrome NOVA Surface Area and Pore Size analyser, after outgassing the samples at 350°C for 3 h under vacuum. Surface area calculations were made using the Brunauer–Emmett-Teller (BET) equation, and the micropore volumes (V_{micro}) and mesopore surface areas (S_{meso}) by the *t*-method. TPR profiles were obtained using a fully automated AMI-200 equipment (Altamira

Instruments), submitted to a 5°C min⁻¹ heating to 700°C under 5% (v/v) H₂ flow diluted in air (total flow=30 cm³ min⁻¹).

XRD has been applied to study the structure of the commercial and ball-milled cellulose samples. To evaluate the degree of crystallinity of cellulose, XRD patterns were recorded by a Philips X'Pert MPD diffractometer (Cu-Ka=0.15406 nm).

2.5. Catalytic experiments

The hydrolytic hydrogenation of cellulose was performed in a 1000 ml stainless steel reactor (Parr Instruments, USA Mod. 5120) equipped with a gas supply system, a manometer, a temperature sensor and a filtered sample outlet, which prevents the catalyst particles to pass through it. In standard tests, 300 ml of water, 750 mg of cellulose and 450 mg of catalyst were introduced into the reactor under stirring at 150 rpm. Then the reactor was flushed three times with N₂ to remove air. After heating under this atmosphere to the desired temperature (205°C), the reaction was initiated by switching from inert gas to H₂ (50 bar). Samples (1 ml) were periodically withdrawn for analysis. After reaction (5 h), the catalyst and non-hydrolysed cellulose were filtered out. The conversion of cellulose was calculated as the ratio of the hydrolysed cellulose mass to its initial amount; the values were also verified on the basis of total organic carbon (TOC) data.

2.6. Product analysis

The quantitative analysis of the samples was carried out by high performance liquid chromatography (HPLC). The chromatograph (Elite LaChrom HITACHI) was equipped with a refractive index (RI) detector and the products were separated in an ion exclusion column (Alltech OA 1000). The retention times and calibration curves were determined by comparison with standard samples. The eluent was a H₂SO₄ solution (0.005 м). An injection volume of 30 μl, a flow rate of 0.5 ml min⁻¹ and a measuring time of 20 min were selected. The samples were injected into the HPLC directly after the experiments without any pre-treatment other than filtering to prevent solid particles from entering the columns. The selectivity (S_i) of each product i at time t was calculated as:

$$S_i = \frac{c_i}{v_i \cdot C_0 \cdot X} \tag{1}$$

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 moles of cellulose consumed, according to the stoichiometry.

For determining the conversion of non-soluble cellulose into water soluble products, TOC data was obtained with a Shimadzu TOC 5000-A and the conversion determined using the equation: X_{TOC}=(moles of total organic carbon in the resultant liquid)/(moles of carbon in cellulose charged into the reactor)×100%. Since the TOC conversion was very close to the weight conversion (differences smaller than 5%), implying that only a small amount of carbon-containing gas was generated, gas products were not considered in our study.

3 Results and discussion

3.1 Materials characterisation

Figure 2 shows that the reduction ranges of Ir and Rh catalysts supported on AC are around 80–150°C. Also, Ru catalyst profile shows a wide reduction peak around 100–250°C, while Pd and Pt present a reduction range around 200–250°C. According to these results, and for comparative purposes, all catalysts were reduced at 250°C to assure effective reduction of the metal.

Analysing the N₂ adsorption isotherms (Figure 3A) it is possible to observe the well-developed microporosity of AC. The textural properties of the Ru/AC catalysts are not significantly different from those of the original support, which presents a specific area of about 850 m² g⁻¹. Moreover, the results show a slight decrease of BET surface area and micropore volume after the impregnation with the metal phase and the increase in metal loading (Table 1). Also, no significant difference is found in the textural
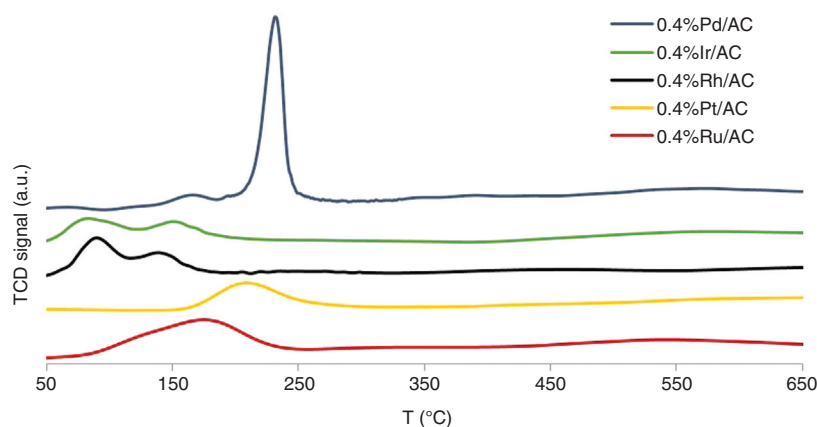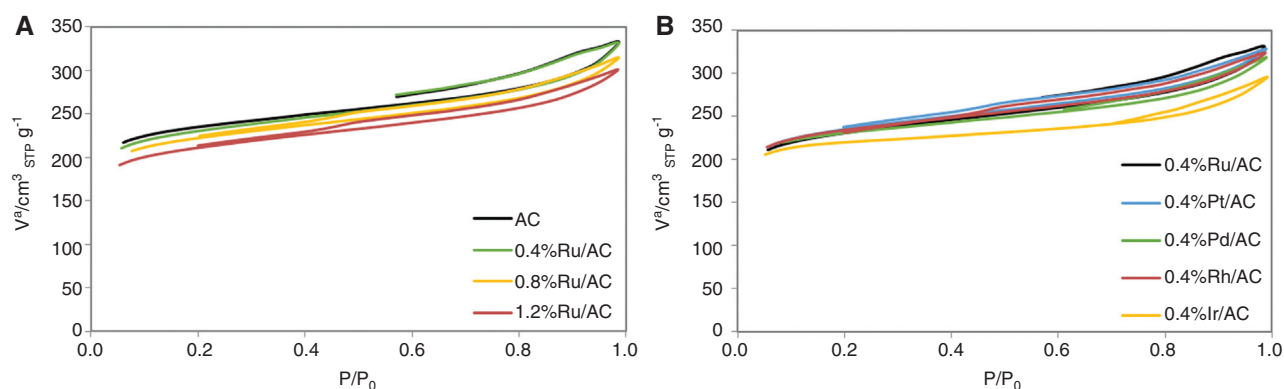

Figure 2: TPR profiles of the prepared catalysts.

Figure 3: N$_2$ adsorption isotherms of (A) the support and Ru catalysts, and (B) the other metal catalysts.

Table 1: Textural properties of the support and the different catalysts.

Sample	S_{BET} (m^2 g^{-1})	S_{meso} (m^2 g^{-1})	V_{micro} (cm^3 g^{-1})
AC	847	152	0.301
0.4% Ru/AC	804	151	0.294
0.8% Ru/AC	791	149	0.281
1.2% Ru/AC	735	145	0.263
0.4% Pt/AC	815	158	0.296
0.4% Pd/AC	793	133	0.300
0.4% Rh/AC	827	146	0.300
0.4% Ir/AC	800	106	0.289

properties of the different metal catalysts (Figure 3B and Table 1).

The XRD peak height method is the most widely used method to determine the CrI, allowing fast comparison of samples [19]. The substrate used in this study was microcrystalline cellulose and the CrI was estimated by XRD analysis according to the following equation:

$$CrI = \frac{I_{002} - I_{amorph}}{I_{002}} \qquad (2)$$

where I_{002} is the maximum intensity of the (002) lattice diffraction (2θ=22.6°) and I_{amorph} is the intensity diffraction at 2θ=18°. I_{002} represents both crystalline and amorphous cellulose whereas I_{amorph} represents amorphous cellulose only.

XRD patterns of microcrystalline and ball-milled cellulose are shown in Figure 4. It is possible to observe the strongest peak at 2θ=22.6°, which originates from the cellulose crystalline plane (002) and also that the intensity of the peaks decrease after ball-milling. The CrI of microcrystalline and ball-milled cellulose were 92 and 87%, respectively, showing that there was a slight decrease in cellulose's degree of crystallinity caused by ball-milling. Clearly, the transformation of microcrystalline cellulose into amorphous cellulose suggests that ball-milling has weakened the hydrogen bond networks within microcrystalline cellulose. Such changes are expected to have great influence on cellulose conversion.
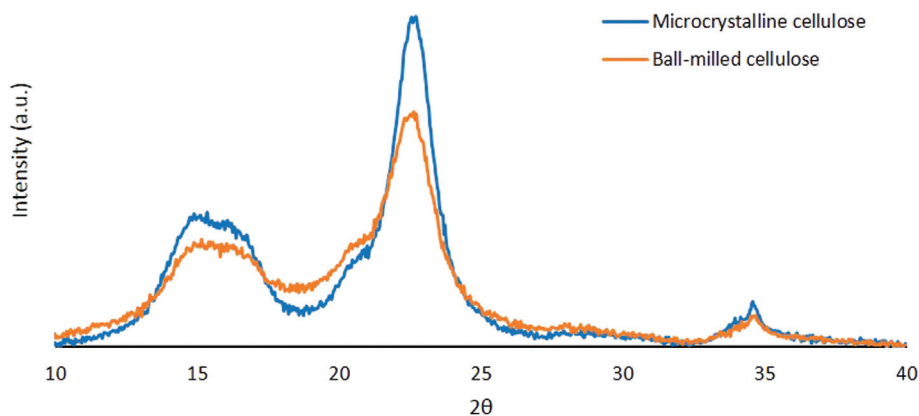

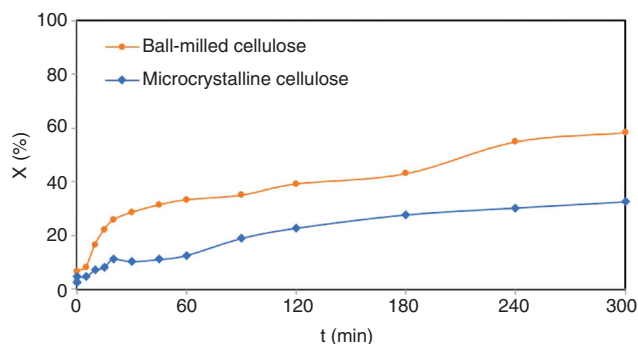**Figure 4:** XRD patterns of microcrystalline and ball-milled cellulose.

Figure 5: Effect of ball-milling in the conversion of cellulose. Reaction conditions: temperature, 205°C; H_2 pressure, 50 bar; cellulose, 750 mg; H_2O, 300 ml; catalyst 0.4% Ru/AC, 450 mg; 150 rpm.

3.2 Catalytic tests

The successful selective transformation of cellulose to sugar alcohols requires the development of catalysts with the ability to promote the coupled hydrolysis/hydrogenation reactions (leading to sorbitol) and also to minimise secondary reactions, which lead to undesirable by-products.

Due to its robust crystalline structure with a linkage of β-1,4-glycosidic and hydrogen bonds, it is difficult to hydrolyse cellulose and transform it into chemicals and fuels. In this work, in order to try to overcome this problem, microcrystalline cellulose was ball-milled. Its effect was analysed in the conversion of cellulose, using an Ru/AC catalyst (0.4% Ru/AC), under the aforementioned conditions (see Section 2.5).

As depicted in Figure 5, ball-milling improved cellulose conversion. In this case, while the hydrolytic hydrogenation of the raw sample (microcrystalline cellulose)

only achieves 32% conversion, that of the ball-milled sample achieves 58% conversion within 5 h of reaction. Moreover, there is a slight increase in the selectivity to sorbitol (from 30 to 35%). Obviously, this must be due to the physical and structural changes in the cellulose induced by ball-milling (shown in the previous section, in Figure 4), which weakens the hydrogen bond network and makes the glucose chains within microcrystalline cellulose more accessible.

According to these results, in the following studies ball-milled cellulose was used instead of microcrystalline (commercial) cellulose. The amount of catalyst was varied between 50 and 450 mg, under the same reaction conditions. In Figure 6, we can observe no significant variation in the conversion of ball-milled cellulose for different amounts of catalyst. However, the selectivity to sorbitol achieves a maximum (45%) when using 300 mg of catalyst (Figure 7). This amount of catalyst was selected for further studies.
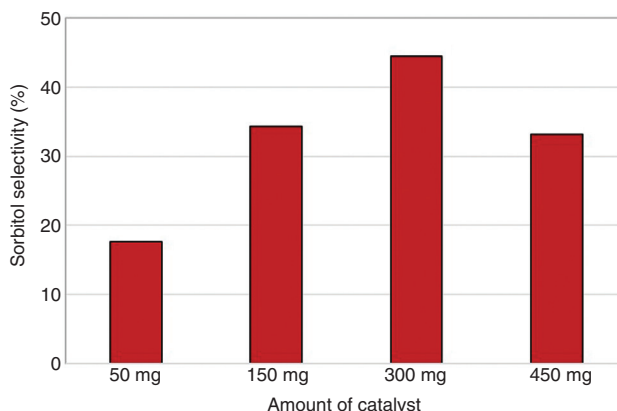

Figure 7: Selectivity of sorbitol using different catalyst amounts, after 5 h of reaction (reaction conditions: see caption of Figure 6).
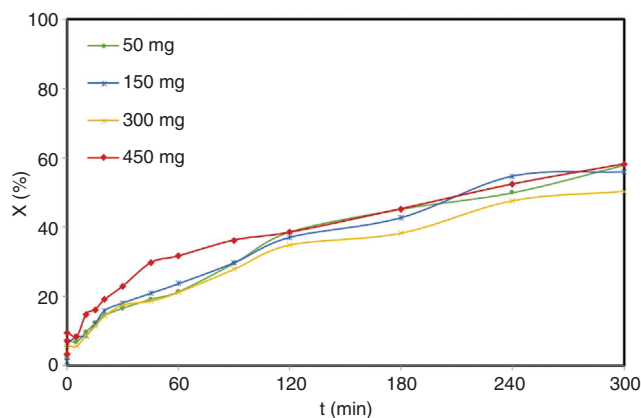

Figure 6: Effect of catalyst amount in the conversion of ball-milled cellulose. Reaction conditions: temperature, 205°C; H_2 pressure, 50 bar; ball-milled cellulose, 750 mg; H_2O, 300 ml; catalyst, 0.4% Ru/AC; 150 rpm.
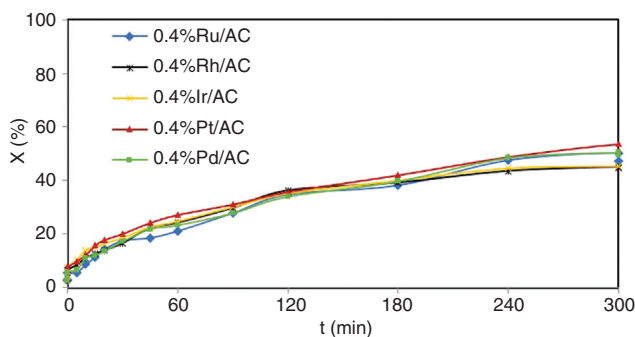

Figure 8: Effect of different catalysts in the conversion of ball-milled cellulose. Reaction conditions: temperature, 205°C; H_2 pressure, 50 bar; ball-milled cellulose, 750 mg; H_2O, 300 ml; catalyst, 300 mg; 150 rpm.
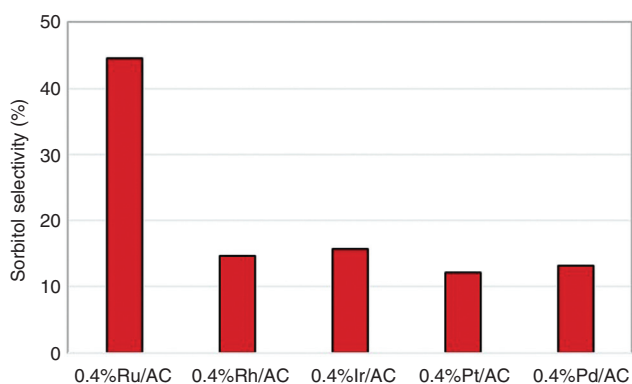
Figure 9: Selectivity of sorbitol using different catalysts, after 5 h of reaction (Reaction conditions: see caption of Figure 8).

Different metals (Pt, Pd, Ir and Rh) supported on AC were also studied as catalysts in the hydrolytic hydrogenation of ball-milled cellulose. Although the conversion of cellulose did not vary significantly (Figure 8), the results obtained show that the Ru catalyst is the most selective to sorbitol (Figure 9). An increase from about 15% to 45% in the selectivity to sorbitol when using the Ru catalyst was observed, which indicates that the other catalysts favour the formation of secondary products.

Figure 10 shows the conversion and the distribution of main products with AC, Ru/AC and Ir/AC as catalysts and without catalyst (blank experiment). It can be seen that for the one-pot reaction, the conversion of cellulose is up to 50% even in the blank condition. If Ru/AC is used, the conversion of cellulose is practically the same as that of AC. However, the selectivity to sorbitol increases greatly.

On the other hand, if Ir/AC is used, both conversion of cellulose and sorbitol selectivity are similar to those obtained in the presence of AC. This tendency is also observed when performing the hydrogenation of glucose. All these results indicate that AC is mainly used as a support material, and only Ru is active for the conversion to sorbitol. As conclusion, the first step – hydrolysis of cellulose to glucose – can be carried out even only with water, while for the second step – hydrogenation of glucose to sorbitol – the presence of an active metal catalyst such as Ru is necessary. As Ru/AC appeared to be the most efficient catalyst, the following step was to vary its metal loading from 0.4 to 1.2%. However, as it can be seen in Figures 11 and 12, both cellulose conversion and sorbitol selectivity decrease with the increase of metal loading, which indicates that in the 0.4%Ru/AC catalyst the metal is probably better dispersed.
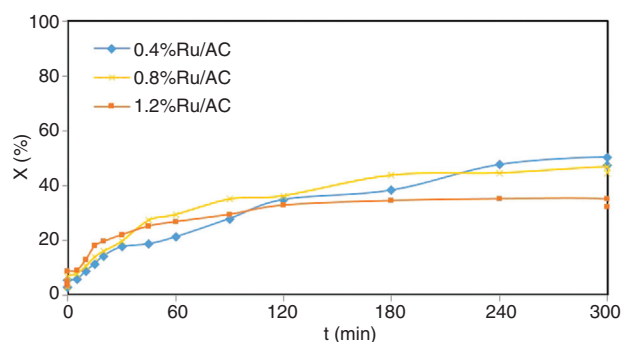

Figure 11: Effect of metal loading in the conversion of ball-milled cellulose. Reaction conditions: temperature, 205°C; H_2 pressure, 50 bar; cellulose, 750 mg; H_2O, 300 ml; catalyst Ru/AC, 300 mg; 150 rpm.
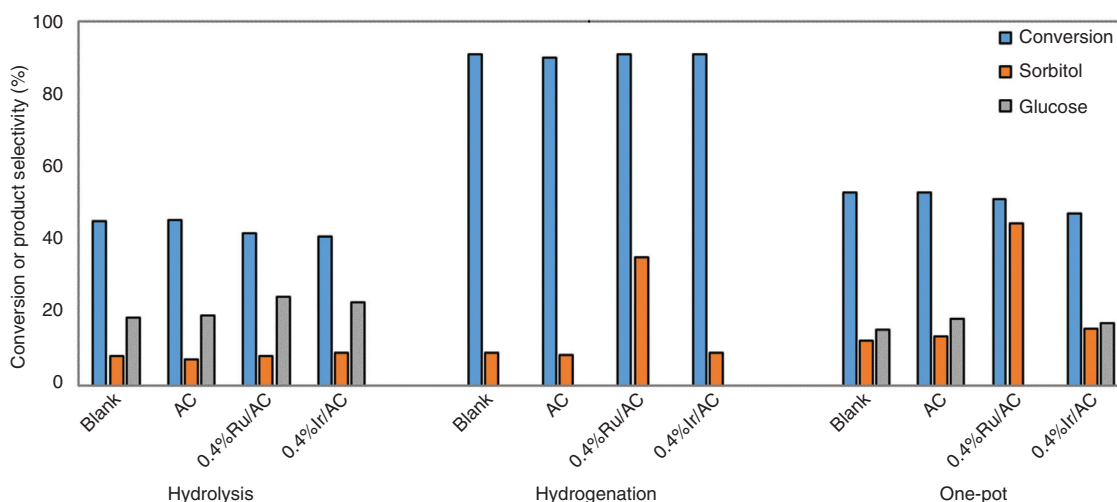

Figure 10: Conversion and distribution of products at different reaction stages after 5 h of reaction (hydrolysis and one-pot conversion) or 1 h of reaction (hydrogenation). Reaction conditions: temperature, 205°C; H_2 pressure (N_2 for hydrolysis), 50 bar; ball-milled cellulose (or glucose in case of hydrogenation), 750 mg; H_2O, 300 ml; catalyst, 450 mg; 150 rpm.
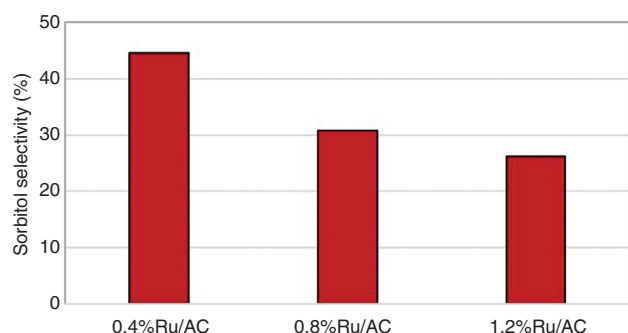
Figure 12: Selectivity of sorbitol for different metal loadings, after 5 h of reaction (Reaction conditions: see caption of Figure 11).

4 Conclusions

Several metal catalysts supported on AC were tested in the one-pot conversion of cellulose. Ru catalysts showed to be highly efficient, particularly if cellulose is ball-milled prior to use in the reaction. Conversion of 32% and a sorbitol selectivity of 30% were obtained after 5 h of reaction in the conversion of microcrystalline cellulose. With an appropriate selection of experimental conditions, higher conversions (over 50%) and selectivities to sorbitol (45%) can be attained when ball-milled cellulose is used.

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Bionotes

Lucília S. Ribeiro

Lucília S. Ribeiro studied Chemical Engineering at the Faculty of Engineering, University of Porto (FEUP), Portugal, where she obtained a MSc degree in 2012. Since 2013, she has been pursuing a PhD in Chemical and Biological Engineering, under the supervision of Dr. Manuel Fernando R. Pereira and Dr. José J. M. Órfão, working on the catalytic conversion of biomass.

José J.M. Órfão

José Joaquim de Melo Órfão obtained his PhD in Chemical Engineering (1987) from the Faculty of Engineering of University of Porto (FEUP). Presently, he is an Associate Professor at FEUP and a senior researcher at the Laboratory of Catalysis and Materials. Most of his research has been focused in the area of carbon materials and their applications in catalysis and adsorption; the development of heterogeneous catalysts for environmental and fine chemistry processes are also included in his main interests. He has authored 124 publications in leading international journals, which have been cited approximately 4600 times.

Manuel Fernando R. Pereira

Manuel Fernando Ribeiro Pereira obtained his PhD in Chemical Engineering from the University of Porto (1998). Currently, he is an Associate Professor at the Faculty of Engineering, University of Porto (FEUP) and a senior researcher at the Laboratory of Catalysis and Materials. His research activities have been focused on the development of carbon materials and catalysts for environmental applications and energy production. He is (co)-author of more than 150 publications in ISI journals (h-index=34).