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Enhanced direct production of sorbitol by cellulose ball-milling

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The catalytic conversion of lignocellulosic biomass to renewable and valuable chemicals has attracted global interest. Given the abundance of this renewable raw material and its reduced impact on the food chain, it is an attractive source for replacing fossil fuels and obtaining chemicals or fuels in the context of a sustainable economy. In this work, a catalyst (Ru/AC) was developed to perform, in a single step, hydrolysis and hydrogenation of cellulose to sorbitol. An activated carbon supported ruthenium catalyst was examined for the one-pot hydrolytic hydrogenation of cellulose and it has shown to be very active and selective for the conversion of cellulose into sorbitol. When microcrystalline cellulose was used, a conversion of 36% was reached after 5 hours of reaction, with a selectivity to sorbitol of 40%. On the other hand, ball-milled cellulose allowed attaining conversions close to 90%, with a selectivity to sorbitol of 50%. Moreover, if the catalyst was ball-milled together with cellulose, the selectivity to sorbitol could be further increased to almost 80%. The catalyst showed excellent stability after repeated use. In this work we combined hydrolysis and hydrogenation in one-pot (using heterogeneous catalysts instead of homogeneous), in the presence of a Ru/AC catalyst (without any support pre-treatment with acids) and pre-treated cellulose just by ball-milling (instead of using acids). For this reason, the results obtained in this work are one of the best values achieved when using supported metal catalysts to convert cellulose by an environmentally friendly process.

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Introduction

Steadily increasing greenhouse gas emissions and worldwide energy demand, together with the limited availability and sustainability of fossil fuels, make it necessary to identify alternatives and develop new environmentally friendly processes on the basis of renewable feedstocks.[1–3] Recently, lignocellulosic biomass, which does not compete with food sources and is widely available as a low cost feedstock, has drawn a lot of attention as one of the most attractive alternatives to replace fossil resources for the production of fuels and fine chemicals.[2–4] Cellulose is the most abundant form of biomass.[5] Therefore, cellulose is the most promising natural resource for the conversion into more valuable chemicals.[4] In the last few decades, many reaction routes have been developed for its use. Among these, the production of polyols, especially sorbitol, *via* cellulose hydrolysis combined with hydrogenation is an important research field (Fig. 1).[6] Sorbitol is a promising platform chemical, which can be used as a dispensing agent and a humectant in pharmaceuticals, cosmetics and textiles.[1] In addition, it is one of the twelve building block chemicals produced from biomass resources[5] and it is also used in the synthesis of surfactants and fine chemicals, such as in the synthesis of vitamin C.[6]

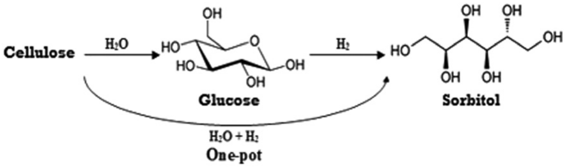

Fig. 1 Catalytic conversion of cellulose into sorbitol.

Due to its robust crystalline structure, the effective degradation of cellulose is still a challenge.[5] Usually, the process for transformation of cellulose consists of its hydrolysis to glucose, followed by the hydrogenation of glucose to polyols. Homogeneous catalysts, such as sulphuric acid, as well as cellulase enzymes promote the production of glucose in high yields from cellulose.[5] However, cellulase is expensive and can hardly be reused;[7] on the other hand, the use of strong liquid acids is not sustainable and suffers from serious drawbacks such as low selectivity, separation of products, corrosion and

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acid recovery or disposal.[7,8] Compared with homogeneous catalysts, heterogeneous solid catalysts have several advantages,[3] such as being easily recovered and reused. Recently, instead of the traditional use of liquid acids, extensive attention has been given to the direct conversion of cellulose to polyols over heterogeneous catalysts.[7,9–12] Ru has been considered a good catalyst for hydrogenation with high activity and is relatively cheap compared to noble metals (such as Pt or Au).[4,8] Carbon materials such as activated carbon and carbon nanotubes are known as heat- and water-tolerant supports.[5] For this reason, carbon supported metal catalysts have been extensively studied.

In 2006, Fukuoka and Dhepe reported the first hydrolytic hydrogenation of cellulose using only solid catalysts, in which Pt/γ-Al_2O_3 promoted the production of sorbitol and mannitol at 25% and 6% yields, respectively.[13] After that, Luo *et al.* reported a cellulose conversion of 86% and a 30% sorbitol yield over a carbon supported ruthenium catalyst (Ru/C) at 245 °C.[14] Since the rate-determining step of the hydrolytic hydrogenation is the hydrolysis of cellulose to glucose,[5] some pre-treatment of cellulose is required in order to facilitate its conversion. Usually, this is achieved with chemical treatments,[15–17] where the crystallinity of cellulose is reduced when it is in contact with acids. For example, Deng *et al.* reported that the crystallinity of cellulose decreased by treating it with phosphoric acid.[18] This group reported the conversion of cellulose with a 69% sorbitol yield,[18] which is, to the best of our knowledge, one of the highest values to date, over a Ru/CNT catalyst using cellulose pre-treated with phosphoric acid at a reaction temperature of 185 °C. Geboers *et al.* used a mixture of Ru/C and heteropoly acid $H_4SiW_{12}O_{40}$ to enhance the hydrolysis rate,[19] which gave 85% yield of sugar alcohols from ball-milled cellulose and 36% yield from microcrystalline cellulose. Though this is one of the best sugar alcohol yields attained to date, it involved the utilization of an acid, which is not such an environmentally friendly approach.

In this work, the pre-treatment of cellulose is done by ball-milling, avoiding the use of acids, and the problems associated with their use (such as disposal).

Results and discussion

Characterizations

The catalyst (0.4%Ru/AC) was initially characterised by temperature programmed reduction (TPR). The TPR profile (Fig. 2) showed a wide reduction peak around 100–250 °C, and so the catalyst was reduced at 250 °C to assure effective reduction of the metal.

By analysing the N_2 adsorption isotherms (Fig. 3) it is possible to observe the well-developed microporosity of the support (AC), which presents a specific area of about 850 $m^2\ g^{-1}$. As expected, no drastic changes in the textural properties of the catalyst were observed. The BET surface area of Ru/AC decreased slightly compared to the unloaded carbon (Table 1). Therefore, it was considered that the textural properties of the supported ruthenium catalyst are not significantly different from those of the original activated carbon.

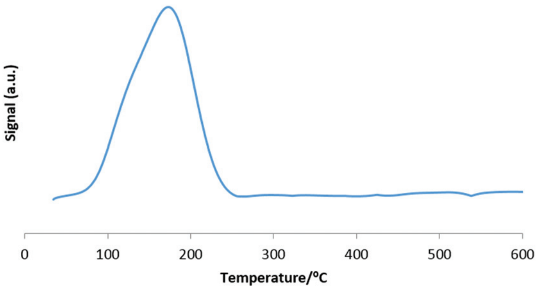

Fig. 2 TPR profile of the catalyst.

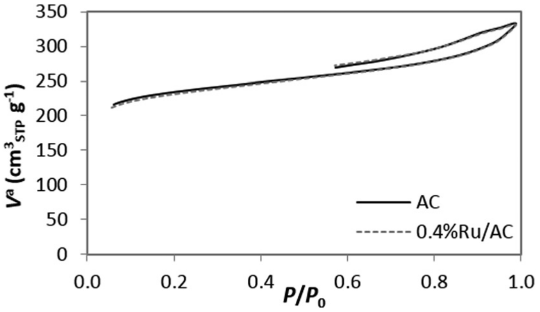

Fig. 3 N_2 adsorption isotherms of the support and catalyst.

Table 1 Textural properties of the support and catalyst

Sample	S_{BET} ($m^2\ g^{-1}$)	S_{meso} ($m^2\ g^{-1}$)	V_{micro} ($cm^3\ g^{-1}$)	Metal loading (wt%) [ICP]	d_M (nm) [TEM]
AC	847	152	0.301	—	—
0.4%Ru/AC	804	151	0.294	0.32 ± 0.02	1.4 ± 0.3

Table 1 also shows the metal loading of the catalyst. The ruthenium content obtained by ICP analysis (0.32%) is slightly lower than the nominal value (0.4%), which indicates that a fraction of ruthenium was not deposited on the support during the preparation step.

TEM micrographs (Fig. 4a) were collected in order to get information about the metal particle size distribution

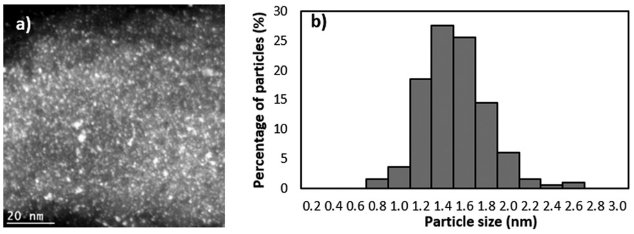

Fig. 4 TEM image (a) and ruthenium particle size distribution on 0.4% Ru/AC (b).

(Fig. 4b). The average crystallite size of the studied catalyst is presented in Table 1. As observed, the incipient wetness method allows obtaining relatively small metal crystallite sizes for the catalyst prepared.

The XRD peak height method is the most widely used method to determine the crystallinity index of cellulose, allowing fast comparison of samples.[5,20] The substrates used in this study were microcrystalline (sample cellulose_f0_t0) and ball-milled cellulose, and the crystallinity index (CrI) was calculated using the following equation:

$$\mathrm{CrI}\ (\%) = \frac{I_{002} - I_{\mathrm{AM}}}{I_{002}} \times 100 \qquad (1)$$

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

XRD patterns of microcrystalline and ball-milled cellulose samples are shown in Fig. 5. It is possible to observe the strongest peak at $2\theta = 22.6°$, which originates from the cellulose crystalline plane (002). As expected and shown in Table 2, after ball-milling, cellulose had a reduced crystallinity compared to the original cellulose. Besides that, a decrease in both crystallite size and crystallinity index with the increase of ball-milling time and frequency can be noticed. For instance, the degree of crystallinity of microcrystalline cellulose decreases from 92 to 23% just by ball-milling at a frequency of 20 Hz for 4 h. Clearly, the transformation of microcrystalline cellulose into amorphous cellulose suggests that ball-milling has weakened the hydrogen bond networks within cellulose. Such changes are expected to have great influence on cellulose conversion.

The degree of polymerization (DP) of cellulose samples was determined by the viscosity method. All measurements were performed at 25.0 ± 0.5 °C using a Cannon–Fenske capillary viscometer (size 50) and cupriethylenediamine (Cuene) as the solvent.[21,22] For each solution (cellulose and solvent), the measurement was repeated three times and the average was considered. By analysing Table 2, we conclude that there is a slight decrease in the DP of cellulose after ball-milling. Despite the small differences between ball-milled cellulose samples, a slight decrease in DP with the increase of ball-milling time and frequency is noticed.

In order to obtain the particle size distributions of the cellulose samples, the particles were classified according to different intervals. The average diameters (d_{av}) for each sample are presented in Table 2, according to the particle size distributions presented in Fig. 6. By analysing Fig. 6a, a decrease in particle size with the increase in ball-milling frequency can be observed (Table 2). In Fig. 6b there is a notable difference between cellulose_f0_t0 and the ball-milled samples. However, no significant difference is observed between samples ball-milled for different times.

The elemental analysis of microcrystalline and ball-milled cellulose samples revealed carbon, hydrogen and oxygen contents of about 44%, 7% and 49%, respectively. Comparing the results obtained for the different samples, we can ascertain that the cellulose structure is not altered by ball-milling. Furthermore, the results are compatible with cellulose's molecular formula, $(C_6H_{10}O_5)_n$.

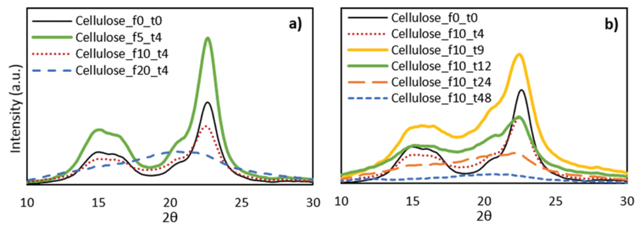

Fig. 5 XRD patterns of cellulose for different ball-milling frequencies (a) and times (b).

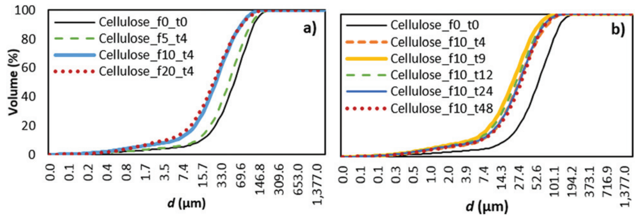

Fig. 6 Particle size distribution for different ball-milling frequencies (a) and times (b).

Table 2 Results for the characterization of the different cellulose samples

	Ball-milling					
Cellulose samples	f (Hz)	t (h)	Crystallite size (nm) [XRD]	CrI (%) [XRD]	DP [Visc.]	d_{av} (nm) [Coulter]
Cellulose_f0_t0	0	0	6.3	92	221	68
Cellulose_f10_t4	10	4	5.4	87	209	37
Cellulose_f10_t9	10	8	5.0	79	207	28
Cellulose_f10_t12	10	12	4.9	76	200	32
Cellulose_f10_t24	10	24	3.1	48	196	35
Cellulose_f10_t48	10	48	2.0	33	191	37
Cellulose_f5_t4	5	4	6.5	93	204	58
Cellulose_f20_t4	20	4	2.0	23	191	36

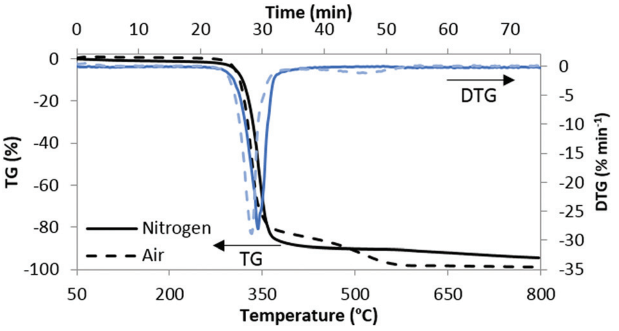

Fig. 7 TG (in black) and DTG (in blue) curves of cellulose decomposition under nitrogen or air.

The mass loss history of microcrystalline cellulose (sample cellulose_f0_t0) under different atmospheres was tracked as shown in Fig. 7. A great mass loss between 290 and 360 °C (almost 90% of total mass) could be found under an inert atmosphere (N_2). Under an oxidative atmosphere (air), a second mass loss was detected at higher temperatures (460–560 °C), with an almost total mass loss above 600 °C. The temperature range corresponding to the first mass loss does not vary regardless of the surrounding atmosphere. These results are consistent with those reported in the literature.[23–25]

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 minimize secondary reactions, which lead to undesirable by-products. For better understanding of this coupled reaction effect, both hydrolysis of cellulose and hydrogenation of glucose were also studied separately, allowing us to conclude that the catalyst influence is mainly in the hydrogenation step.

Preliminary studies were carried out by varying the stirring rate and it was found that under the selected conditions (see the Catalytic experiments section) there were no external diffusional limitations. Blank experiments were performed under the same conditions; the conversion of microcrystalline cellulose was up to 20% without any catalyst. In the presence of AC, the cellulose conversion reached 25% with a selectivity to sorbitol of 15%.

The Ru/AC catalyst gave 36% conversion with a selectivity to sorbitol of 40% after 5 h (Table 3, entry 1).

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 overcome this problem, microcrystalline cellulose was pre-treated by ball-milling. The effect of ball-milling was analysed in the conversion of cellulose, using an activated carbon supported ruthenium catalyst (0.4% Ru/AC).

The effect of ball-milling on cellulose conversion was studied for different times and frequencies as depicted in Fig. 8. While the hydrolytic hydrogenation of the raw sample (cellulose_f0_t0) only achieves 36% conversion, the ball-milled sample cellulose_f10_t48 achieves up to 90% conversion within 5 h of reaction. Moreover, there is also an important increase in the selectivity to sorbitol (Table 3). An increase in both catalytic activity and sorbitol selectivity is noticed not only for increased ball-milling times (entries 2–6), but also for increased ball-milling frequencies (entries 2, 7 and 8), which is consistent with the XRD results. Obviously, this must be due to the physical and structural changes in the cellulose induced by ball-milling, making glucose chains within cellulose more accessible.

Table 3 Comparison between activities (TOFs), conversions of cellulose (*X*) and selectivities (*S*) and yields (*Y*) of sorbitol obtained after 1 and 5 h of reaction[a]

		1 h of reaction				5 h of reaction				
Entry	Substrate	TOF[d] (h^{-1})	X (%)	$S_{sorbitol}$ (%)	$Y_{sorbitol}$ (%)	X (%)	$S_{sorbitol}$ (%)	$Y_{sorbitol}$ (%)	$S_{glucose}$ (%)	$S_{mannitol}$ (%)
1	Cellulose_f0_t0	0.39	16.9	59.5	10.0	35.7	40.5	14.5	2.1	0.5
2	Cellulose_f10_t4	0.49	21.2	66.3	14.1	50.3	44.5	22.4	15.0	1.7
3	Cellulose_f10_t9	0.72	30.6	50.8	15.5	57.2	43.9	25.1	13.1	3.4
4	Cellulose_f10_t12	0.84	32.9	56.5	18.6	62.9	49.6	31.2	11.7	2.9
5	Cellulose_f10_t24	1.29	51.7	48.8	25.2	76.4	49.5	37.8	8.9	3.9
6	Cellulose_f10_t48	1.53	60.1	52.2	31.4	90.8	49.8	45.2	8.5	4.2
7	Cellulose_f5_t4	0.32	14.0	69.8	9.8	38.8	38.4	14.9	0.9	0.5
8	Cellulose_f20_t4	1.57	61.1	42.8	26.1	87.8	48.0	42.1	8.5	3.4
9[b]	(Cellulose + catalyst)_f20_t4	2.00	76.4	89.0	68.0	89.4	76.9	68.8	0.0	4.2
10[c]	Cellulose_f20_t4 + catalyst_f20_t4	1.60	61.4	80.5	49.4	82.1	79.9	65.6	0.0	4.6

[a] Conditions: cellulose (0.75 g), water (300 mL), 0.4%Ru/AC catalyst (0.3 g), 205 °C, 50 bar H_2, 150 rpm. [b] Cellulose and catalyst were ball-milled together at 20 Hz for 4 h (sample denoted as (cellulose + catalyst)_f20_t4). [c] Besides cellulose (Cellulose_f20_t4), the catalyst was ball-milled too under the same conditions (20 Hz for 4 h) and denoted as catalyst_f20_t4. [d] TOF (h^{-1}) = (mole of cellulose converted after 1 h)/(reaction time (= 1 h) × mole of ruthenium active sites); the amount of Ru active sites was calculated from $(6 \times y \times n_s \times W_{cat})/(d_M \times \rho \times N)$, where y and d_M are the Ru weight fraction (from ICP) and the average particle diameter (from TEM), respectively; ρ and n_s are the density of Ru and the number of Ru atoms per unit of area, respectively; W_{cat} is the catalyst mass used in the experiments (0.3 g); and N is the Avogadro number.

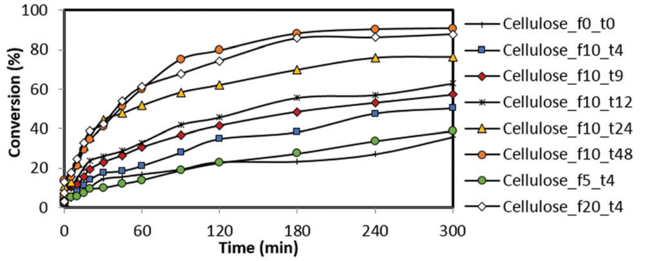

Fig. 8 Evolution of cellulose conversion for different ball-milling times and frequencies.

The results shown in Table 3 also indicate a decrease in sorbitol selectivity with reaction time when using as substrate cellulose samples with higher crystallinity degrees (entries 1–4 and 7). If the cellulose crystallinity index is less than 50% (entries 5, 6 and 8), no significant difference is found in sorbitol selectivity after 1 and 5 h of reaction.

In terms of the effect of ball-milling time, a clear increment in the activity is observed between microcrystalline cellulose (cellulose_f0_t0) and cellulose ball-milled for 48 h (0.39 to 1.53 h^{-1}). When comparing microcrystalline cellulose and cellulose ball-milled at a frequency of 20 Hz (cellulose_f20_t4) there is also an increase of activity from 0.39 to 1.57 h^{-1}. These variations are directly related to the decrease in cellulose crystallinity caused by the increase in ball-milling time and frequency. Indeed, if we plot the activity (TOF) as function of the crystallinity index (CrI) of cellulose, a strong correlation is obtained as shown in Fig. 9.

As already mentioned, since the rate-determining step of the hydrolytic hydrogenation is the hydrolysis of cellulose to glucose, this step is of great importance. So, according to Kobayashi *et al.*, who considered that the hydrolysis of cellulose promoted by carbon catalysts also occurs at the solid–solid interface, the number of collisions is a major obstacle in this type of reaction.[26] Therefore, cellulose and catalyst were ball-milled together (sample denoted as (cellulose + catalyst) _f20_t4) as a pre-treatment to improve the contact between the cellulose and the catalyst, as the mixed state can continue in the subsequent hydrolysis reaction thanks to the insoluble properties of the catalyst and the substrate. The hydrolytic hydrogenation of this mixed sample resulted in 76% conversion after just 1 h of reaction, with 68% yield of sorbitol (Table 3, entry 9), whereas the separately ball-milled catalyst (catalyst_f20_t4) and cellulose (cellulose_f20_t4) provided only 49% yield of sorbitol after 1 h of reaction (entry 10). Also, a great increase in the initial reaction rate by the procedure mentioned above can be observed in Fig. 10. These results indicate that the mix-milling pre-treatment accelerates the hydrolytic hydrogenation of cellulose (compare entries 8–10 in Table 3). Similar results were obtained by Kobayashi *et al.* for the conversion of mix-milled activated carbon and cellulose,[26] which allowed concluding that the enhancement of the reaction performance by mix-milling is not due to the mechano-catalytic hydrolysis during the treatment but due to mixing.

Finally, a very important characteristic for commercial feasibility is the long-term stability of the heterogeneous catalyst. Thus, to test the catalyst deactivation for cellulose conversion into sorbitol, four successive tests under the same conditions were carried out, after sample washing and drying, as shown in Fig. 11. Due to some losses during the catalyst filtration at the end of the reaction, a small amount of fresh catalyst (<5 wt %) was added to the reaction mixture before each run. The conversion of ball-milled cellulose (sample cellulose_f20_t4) was maintained around 88% after 5 h in each run, as well as the selectivity to sorbitol, which was kept almost constant around 47%. Since the cellulose conversion and sorbitol selectivity showed no difference up to the 4th cycle, this indi-

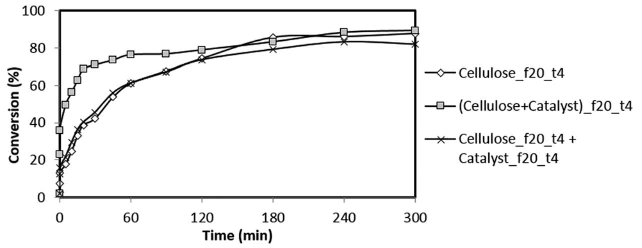

Fig. 10 Evolution of the conversion of cellulose ball-milled apart/together with the catalyst.

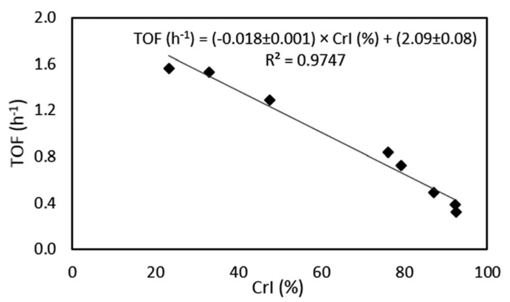

Fig. 9 Correlation between the catalytic activity and the crystallinity index of cellulose.

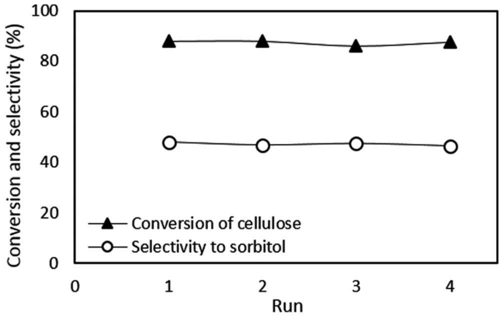

Fig. 11 Recycling test of 0.4% Ru/AC catalyst on the conversion of ball-milled cellulose (cellulose_f20_t4) after 5 h of reaction.

cates that 0.4% Ru/AC exhibits no deactivation and presents excellent stability.

In summary, according to the presented results, cellulose conversions around 90% and sorbitol yields near 45% can be reached after 5 h of reaction if cellulose is pre-treated by ball-milling for 48 h at a frequency of 10 Hz or for 4 h at a frequency of 20 Hz. Moreover, the sorbitol yield can be raised to almost 70% in just 1 h of reaction if the catalyst is ball-milled together with cellulose for 4 h at a frequency of 20 Hz. In addition, the catalyst showed excellent stability after repeated use. Although the comparison between the results obtained in this work and those reported in the literature is particularly difficult since the reaction conditions changed from author to author, to the best of our knowledge, this work reports one of the highest sorbitol yields ever attained without the use of non-environmentally friendly approaches.

Experimental

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. The metal precursor $RuCl_3$ (99.9%, Ru 38%) was also supplied by Alfa Aesar. Activated carbon GAC 1240 PLUS was provided by Norit and sulphuric acid (95%) was obtained from VWR.

Cellulose pre-treatment

The crystal structure and hydrogen bonding in cellulose limit the access to β-1,4-glycosidic bonds by reactants and catalysts.[27] So, in order to facilitate the contact with the catalysts, the crystalline structure of cellulose has to be considered. Mechanical (milling, grinding, steaming and irradiation) and chemical (dissolution, alkali, acid, swelling, gas, oxidation and solvent) treatments decrease the degree of crystallization of cellulose, and this value can be determined by X-ray Diffraction (XRD), ^{13}C NMR and other methods.[17] 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.[5] Acid treatments are the chemical treatments often used for this purpose, but are undesirable due to reactor corrosion and environmental toxicity. In contrast, ball-milling does not suffer from this problem, making it a great alternative to break the robust crystalline structure of cellulose and decrease its crystallinity in a sustainable way.

In this work, microcrystalline cellulose was ball-milled in a ceramic pot with two ZrO_2 balls (12 mm of diameter), in order to reduce its crystallinity before the reaction and study its effect on the performance of the process. The ball-milled cellulose was prepared using a laboratory ball mill (Retsch Mixer Mill MM200) by introducing 1.5 g of commercial microcrystalline cellulose into the ceramic pot, operating at a frequency of 10 Hz for 4 h. This sample was denoted as cellulose_f10_t4. Different ball-milled cellulose samples were prepared by varying the ball-milling frequencies (from 5 to 20 Hz) for 4 h or by varying the ball-milling times (from 4 to 48 h) at a frequency of 10 Hz. These samples were denoted as cellulose_frequency/Hz_time/h, according to the respective ball-milling frequency and time. Following this notation, microcrystalline cellulose was denoted as cellulose_f0_t0, since it was not ball-milled. The crystallinity index of the prepared cellulose samples was determined by XRD.

Preparation of catalysts

A commercial Norit GAC 1240 activated carbon (AC) sample was used as a support for this study. A Ru-based catalyst was prepared by incipient wetness impregnation of AC (sieved between 0.1 and 0.3 mm) 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 into an ultrasonic bath for 30 minutes. 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 for 90 minutes, after which the catalyst was dried overnight in an oven at 110 °C and then stored for later 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). 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.

Characterization of materials

Both the support and the catalyst were characterized by N_2 adsorption at −196 °C 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. The TPR profile was obtained by using a fully automated AMI-200 equipment (Altamira Instruments); the sample was subjected to a 5 °C min^{-1} heating to 700 °C under 5% (v/v) H_2 flow diluted in He (total flow rate = 30 cm^3 min^{-1}). The metal loading of the catalyst was determined in duplicate by inductively coupled plasma-optical emission spectroscopy (ICP/OES), using a PerkinElmer Optima 4300 DV spectrometer. Electron micrographs of the catalyst were acquired with a JEOL2010F instrument equipped with an energy dispersive X-ray spectroscopy detector. Size distributions were determined by the measurement of 200 nanoparticles and the average diameter was calculated by $d_{\text{M}} = \frac{\sum d_i n_i}{\sum n_i}$, where n_i is the number of particles with diameter d_i.

To evaluate the crystallinity index (CrI) of the microcrystalline and ball-milled cellulose samples, XRD patterns were recorded by using a Philips X'Pert MPD diffractometer (Cu-Kα

= 0.15406 nm). The diffracted intensity of Cu-Kα radiation was measured in a 2θ range between 10° and 50°. The degree of polymerization (DP) of cellulose was determined by viscosity measured at 25.0 ± 0.5 °C using a Cannon-Fenske capillary viscometer and cupriethylenediamine (Cuene) as the solvent. The particle-size distribution of each cellulose sample was determined with a Beckman Coulter LS230 Laser Diffraction Particle Size Analyzer with small volume module plus. Elemental analysis was performed on an EA1108 CHNS-O elemental analyser from Carlo Erba Instruments. TG analysis was carried out under nitrogen and air, with a heating ramp of 10 °C min^{-1} from 50 to 800 °C, using an STA 409 PC/4/H Luxx Netzsch thermal analyser.

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 sample outlet with a filter, which prevents the catalyst particles to pass through it. In standard tests, 300 mL of water, 750 mg of cellulose and 300 mg of catalyst (0.4%Ru/AC) were introduced into the reactor under stirring at 150 rpm. Then the reactor was flushed three times with N_2 to remove air. After heating under this atmosphere to the desired temperature (205 °C), the reaction was initiated by switching from an inert gas to H_2 (50 bar). Samples (1 mL) were periodically withdrawn for analysis. After the reaction, 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.

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 H_2SO_4 solution (0.005 M). 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 column. The selectivity (S_i) of each product i at time t was calculated as:

$$S_i = \frac{C_i}{\nu_i C_0 X} \tag{2}$$

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 ν_i corresponds to the moles of i produced per mole of cellulose consumed, according to the stoichiometry. The yield (Y_i) of each product i at time t was determined as the product between the corresponding selectivity and cellulose conversion.

For determining the conversion of non-soluble cellulose into water soluble products, TOC data were obtained with a Shimadzu TOC 5000-A and the conversion was determined using the equation: X_{TOC} = (moles of total organic carbon in the resulting 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, and gas products were not considered in our study.

Conclusions

A Ru catalyst supported on activated carbon was tested in the one-pot conversion of cellulose. The catalyst showed to be highly efficient, particularly if cellulose is ball-milled prior to use in the reaction. Moreover, if the catalyst was ball-milled together with cellulose, the selectivity to sorbitol could be further increased. Ball-milling allowed decreasing the crystallite size and crystallinity index of cellulose, without significantly changing its polymerization degree. As expected, the catalytic activity and sorbitol yield increased with the increase in ball-milling time and frequency, as a consequence of the decrease in cellulose crystallinity. A strong correlation between the catalytic activity and cellulose crystallinity was found. In addition, no obvious deactivation was observed after several runs. To the best of our knowledge, this article presents one of the best results ever attained for the direct conversion of cellulose into sorbitol using such a green process.

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Notes and references

1 A. M. Ruppert, K. Weinberg and R. Palkovits, *Angew. Chem., Int. Ed.*, 2012, **51**, 2564.

2 D. M. Alonso, S. G. Wettstein and J. A. Dumesic, *Chem. Soc. Rev.*, 2012, **41**, 7965.

3 C.-H. Zhou, X. Xia, C.-X. Lin, D.-S. Tong and J. Beltramini, *Chem. Soc. Rev.*, 2011, **40**, 5588.

4 J. W. Han and H. Lee, *Catal. Commun.*, 2012, **19**, 115.

5 M. Yabushita, H. Kobayashi and A. Fukuoka, *Appl. Catal., B*, 2014, **145**, 1.

6 J. Xi, Y. Zhang, Q. Xia, X. Liu, J. Ren, G. Lu and Y. Wang, *Appl. Catal., A*, 2013, **459**, 52.

7 X. Wang, L. Meng, F. Wu, Y. Jiang, L. Wang and X. Mu, *Green Chem.*, 2012, **14**, 758.

8 H. Wang, L. Zhu, S. Peng, F. Peng, H. Yu and J. Yang, *Renewable Sustainable Energy Rev.*, 2012, **37**, 192.

9 A. Negoi, K. Triantafyllidis, V. I. Parvulescu and S. M. Coman, *Catal. Today*, 2014, **223**, 122.

10 H. Kobayashi, Y. Ito, T. Komanoya, Y. Hosaka, P. L. Dhepe, K. Kasai, K. Hara and A. Fukuoka, *Green Chem.*, 2011, **13**, 326.

11 P. Dhepe and A. Fukuoka, *ChemSusChem*, 2008, **1**, 969.

12 M. Käldström, N. Kumar and D. Y. Murzin, *Catal. Today*, 2011, **167**, 91.

13 A. Fukuoka and P. Dhepe, *Angew. Chem., Int. Ed.*, 2006, **45**, 5161.

14 C. Luo, S. Wang and H. Liu, *Angew. Chem., Int. Ed.*, 2007, **46**, 7636.

15 V. B. Agbor, N. Cicek, R. Sparling, A. Berlin and D. B. Levin, *Biotechnol. Adv.*, 2011, **29**, 675.

16 P. Kumar, D. M. Barrett, M. J. Delwiche and P. Stroeve, *Ind. Eng. Chem. Res.*, 2009, **48**, 3713.

17 P. Yang, H. Kobayashi and A. Fukuoka, *Chin. J. Catal.*, 2011, **32**, 716.

18 W. Deng, X. Tan, W. Fang, Q. Zhang and Y. Wang, *Catal. Lett.*, 2009, **133**, 167.

19 J. Geboers, S. Van de Vyver, K. Carpentier, K. de Blochouse, P. Jacobs and B. Sels, *Chem. Commun.*, 2010, **46**, 3577.

20 S. Park, J. Baker, M. Himmel, P. Parilla and D. Johnson, *Biotechnol. Biofuels*, 2010, **3**, 1.

21 B. B. Hallac and A. J. Ragauskas, *Biofuels, Bioprod. Biorefin.*, 2011, **5**, 215.

22 M. L. R. Medina and V. Kumar, *Int. J. Pharm.*, 2007, **337**, 202.

23 J. J. M. Orfão, F. J. A. Antunes and J. L. Figueiredo, *Fuel*, 1999, **78**, 349.

24 S. Sivasangar, Y. H. Taufiq-Yap, Z. Zainal and K. Kitagawa, *Int. J. Hydrogen Energy*, 2013, **38**, 16011.

25 D. Shen, J. Ye, R. Xiao and H. Zhang, *Carbohydr. Polym.*, 2013, **98**, 514.

26 H. Kobayashi, M. Yabushita, T. Komanoya, K. Hara, I. Fujita and A. Fukuoka, *ACS Catal.*, 2013, **3**, 581.

27 H. Zhao, J. H. Kwak, Y. Wang, J. A. Franz, J. M. White and J. E. Holladay, *Energy Fuels*, 2005, **20**, 807.