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A one-pot method for the enhanced production of xylitol directly from hemicellulose (corncob xylan)

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An efficient one-pot reaction system for converting hemicellulose (corncob xylan) into xylitol was developed by using a heterogeneous catalyst and water as solvent, without the presence of any acids. A xylitol yield of 46.3% was achieved after 45 min of reaction using Ru/CNT as catalyst, which showed excellent stability after repeated use. Since the conversion of hemicellulose consists of xylan hydrolysis to xylose followed by the subsequent hydrogenation to xylitol, the two steps were then evaluated separately. The effect of the presence of cellulose on the conversion of xylan and distribution of products was also studied and the yield of xylitol was increased up to around 60% in less than 1 h of reaction. Furthermore, a yield of sorbitol over 80% could also be attained in just 2 h of reaction. Being this result one of the best ever reported for the direct conversion of cellulose and hemicellulose using an environmentally friendly approach, the proposed method shows great potential for the optimization of the catalytic production of xylitol and sorbitol.

Introduction

Lignocellulosic biomass is an abundant renewable resource and its transformation into valuable products that can replace those derived from petrochemical sources is very attractive for the sustainable supply of fine chemicals and fuels^{1,2}. Lignocelluloses are generally composed of cellulose (40-50%), hemicelluloses (25-35%) and lignin (15-20%)^{1,3}. Xylan is the main component of hemicelluloses and its most potential sources include agricultural crops, such as straw, sugar cane and corn stalks and cobs⁴⁻⁶. Although extensive efforts have been made for the conversion of cellulose^{7,8}, a less number of works have been developed for the conversion of hemicelluloses^{9,10}. So, in comparison to the one-pot process that has been developed for the conversion of cellulose. the hydrolytic hydrogenation of hemicelluloses into sugar alcohols is of great interest (Figure 1), since their branched structure and lower degree of polymerization makes them easily hydrolysed^{2,11}. While the conversion of hemicelluloses into furfural has been extensively described¹²⁻¹⁶, the formation of other interesting and even more valuable chemicals, like xylitol¹⁷⁻¹⁹, is less frequent. Xylitol, a natural occurring five carbon sugar alcohol, is on the top 11 high added-value products that can be obtained from biomass^{17,19,20}. Due to its properties of low energy and inhibition against the metabolism of dental plaque formation, xylitol has been

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widely used in oral hygiene and pharmaceutical products^{6,19,21}. Additionally, xylitol is water-soluble, does not caramelize at elevated temperatures, presents a sweeting capacity 1.2 times higher than white sugar (sucrose) and 40% less calories and also has lower insulin requirements, working as a substitute for diabetics^{17,21}. So, xylitol is one of the most interesting products to be directly obtained from xylan. In the case of the one-pot conversion of cellulose, sorbitol appears as one of the most important products, 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 and vitamin C²². Therefore, the development of an efficient and single step process



for the conversion of hemicelluloses into xylitol using only water as solvent in the presence of hydrogen is of great importance¹¹.

Figure 1. One-pot hydrolytic hydrogenation of cellulose and hemicellulose.

Dhepe and Sahu reported for the first time a one-pot process for the conversion of solid hemicellulose into xylose, arabinose and furfural using solid acid catalysts in aqueous media¹⁶. Since then,

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some works have reported the hydrolytic hydrogenation of arabinogalactans^{2,11}, but only a few have addressed the conversion of xylans^{17,23}. Inspired by Kobayashi et al. previous work using an alcohol as hydrogen source for the conversion of cellulose into sorbitol and mannitol²⁴, Yi and Zhang developed a one-pot process for the selective conversion of hemicellulose (xylan) to xylitol via transfer hydrogenation¹⁷. They achieved a xylitol yield of 81.8% after 3 h using isopropanol instead of H₂ high-pressure. However, in these conditions, they found out that a small amount of sulphuric acid was crucial for the conversion of hemicellulose into xylitol, attaining a yield of xylitol of only 5.7% in the absence of any acidic additive. More recently, Liu et al. also studied the conversion of xylan into xylitol and obtained a yield of 79% after 12 h of reaction at 200 °C and 60 bar of H₂, using a Ir-ReOx/SiO₂ catalyst combined with H₂SO₄²³.

To the best of our knowledge, the number of studies dealing with the direct production of xylitol from xylan by heterogeneous catalysis is very limited, and the effect of many variables on the catalytic activity of the catalyst still remains an open question. For these reasons, this paper reports a new approach for xylitol production from hemicellulose (corncob xylan), evaluating the role of the catalyst in terms of xylitol yield from xylose and xylan, and avoiding the use of acids (and the problems associated with their use, such as disposal), with the aim of designing a green catalytic pathway for the development of a sustainable xylitol production.

Results and discussion

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Characterization of materials.

The catalyst was firstly characterized by temperature programmed reduction (TPR) under H_2 to determine the appropriate temperature of reduction of the metal. The TPR profile obtained showed a reduction peak around 200-300 °C, and so the catalyst was reduced at 250 °C for 3 h to assure effective reduction of the metal²⁵.

The carbon nanotubes (CNT) sample shows a N_2 adsorption isotherm of type II (Figure 2), which is typical of non-microporous materials. The BET surface area of the Ru/CNT catalyst decreased slightly compared to the support (Table 1). Therefore, it was assumed that the textural properties of the catalyst are not significantly different from those of the support.



Figure 2. N₂ adsorption isotherms of the support and catalyst.

Table 1. Textural properties of the support and catalyst.

	•				
Sample	SBET	S _{meso}	V _{micro}	<i>d</i> _M (nm)	D (%)
	(m²⋅g⁻¹)	(m²⋅g⁻¹)	(cm³·g⁻¹)	[TEM]	[TEM]
CNT	267	267	0	-	-
Ru/CNT	245	245	0	1.0 ± 0.1	74

The average crystallite size ($d_{\rm M}$) and metal dispersion (*D*) of Ru/CNT are included in Table 1 (see Figure S1). The impregnation method used allows obtaining relatively small metal crystallite sizes with a good metal dispersion throughout the carbon nanotubes²⁵.

Thermogravimetric analysis allowed tracking the mass loss histories of cellulose and hemicellulose (xylan) under different atmospheres as shown in Figure 3. Cellulose presented a great mass loss between 290 and 360 °C under inert atmosphere (N2), corresponding to a loss around 90% of the total mass (Figure 3a)²⁶. Under oxidative atmosphere (air), another mass loss was detected for higher temperatures (450-550 °C), due to the oxidation of the char. Thermal analysis of xylan demonstrated a first event in the range of 70-100 °C due to dehydration. The second and most relevant loss of 70% appeared in the range of 220 and 360 °C due to polymer decomposition. Total mass losses close to 100% above 600 °C were achieved under oxidative atmosphere for both materials, so there was almost no residue left at the end. The temperature range that corresponds to the first mass loss did not vary with the surrounding environment. The results obtained are consistent with those reported in literature^{27,28}.





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First derivatives of the thermograms were calculated and are also represented in Figure 3 to highlight the inflexion points that indicate thermal transitions under the different atmospheres. Xylan starts decomposing at slightly lower temperatures than cellulose, but the corresponding differential thermogravimetry (DTG) curves are similar in both inert and oxidative atmospheres. Cellulose presents a transition peak around 330 °C in both atmospheres. For xylan, the transition peak is around 300 °C and there can also be observed an extra peak which can be attributed to the presence of non-cellulosic impurities.

The elemental analysis of cellulose and hemicellulose revealed carbon, hydrogen and oxygen contents of about 42-44%, 6-7% and 49-52%, respectively (Table 2). The results obtained are compatible with cellulose and hemicellulose's molecular formulas, $(C_6H_{10}O_5)_n$ and $(C_5H_8O_4)_m$, respectively.

Table 2. Elemental analysis results for microcrystalline cellulose and xylan.²⁶

Sample	С	Н	0
Cellulose ^a	44.5	6.2	49.3
Hemicellulose ^a	45.5	6.1	48.4
MC-cellulose ^b	(44.2 ± 0.1)%	(6.9 ± 0.1)%	(48.9 ± 0.3)%
Xylan⁵	(41.7 ± 0.3)%	(5.9 ± 0.1)%	(52.4 ± 0.9)%
3	h		

^aTheoretical values. ^bMeasured values.

Xylitol production from corncob xylan.

The hydrolytic hydrogenation of hemicellulose over heterogeneous catalysts leads to a large spectrum of products. The direct conversion of corncob xylan to xylitol was evaluated using Ru/CNT as catalyst under the conditions described in the Catalytic experiments section. These conditions were chosen in order to evaluate the reaction for the one-pot hydrolytic hydrogenation of hemicellulose (xylan) and to facilitate the comparison with the conversion of cellulose under similar reaction conditions, previously reported²⁵. The results depicted in Figure 4 indicate that the catalyst can efficiently convert xylan to xylitol in one-step via combined hydrolysis and hydrogenation. Due to its non-crystalline structure, the conversion of xylan is quite fast, contrary to cellulose, and a conversion of 100% was easily reached in just 5 min of reaction. The xylose concentration and xylan conversion at the beginning of the reaction in Figure 4 are not zero since t = 0corresponds to the introduction of hydrogen into the system; there was a previous heating to 205 °C under nitrogen that took about 1 h and 45 min (see the Catalytic experiments section), which was enough for the hydrolysis of xylan to xylose (see Figure S2). From this instant, the reaction was performed under hydrogen atmosphere and the xylose produced started to convert into xylitol. A great decrease in the yield of xylose can be observed during the first 30 min of reaction, accompanied by an increase in the yield of xylitol, which reached a maximum of 46.3% after 45 min of reaction. After this time, a decrease in the yield of xylitol was noticed, due to its further conversion to other undesirable compounds. Other products were detected, such as sorbitol, formic acid, ethylene glycol (EG) and propylene glycol (PG), but with yields lower than 5%, which are almost constant during the 5 h of

reaction. The pH of the reaction mixture was also measured and a decrease from around 7 to 5 was observed from the beginning to the end of the reaction, indicating a possible formation of acid by-products during the reaction time.

The reuse of the catalyst was performed for the one-pot conversion of xylan. After reaction, the catalyst was recovered by filtration of the final reaction mixture, washed with deionized water and dried overnight in an oven. Due to some losses during the filtration, a small amount of fresh catalyst (< 5 wt. %) was added to the reaction mixture before each run. Four successive tests were carried out under the same conditions and the results are shown in Figure 5. A conversion of xylan of 100% was achieved after 5 min of reaction in each run and the yield of xylitol after 30 min of reaction was kept almost constant around 43-46%. These results indicate that the Ru/CNT catalyst exhibits almost no deactivation and presents excellent stability.



Figure 4. Conversion of xylan and yields of xylose and xylitol with the reaction time. Reaction conditions: xylan (0.75 g), water (300 mL), 0.4%Ru/CNT (0.3 g), 205 °C, 50 bar H₂, 150 rpm.



Figure 5. Successive tests of Ru/CNT on the conversion of xylan to xylitol after 30 min of reaction. Reaction conditions: xylan (0.75 g), water (300 mL), 0.4%Ru/CNT (0.3 g), 205 °C, 50 bar H₂, 150 rpm.

Following the same procedure used for the one-pot conversion of cellulose to sugar alcohols²⁶, the direct conversion of hemicellulose comprises two steps: the hydrolysis of hemicellulose to sugars followed by their hydrogenation to sugar alcohols. Table 3 shows the conversion of xylan and distribution of products with CNT and Ru/CNT as catalysts and also without any catalyst (blank experiment). It can be seen that after 30 min of reaction the conversion of xylan is close to 100% even without any catalyst. However, no sugar alcohols (<10%) could be detected. In this

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Table 3. Xylan conversion and yield of products with CNT and Ru/CNT as catalysts, after 30 min of reaction.*

Catalyst	X _{xylan} ± 3 (%) -	Product yield ± 0.8 (%)					
		Xylose	Xylitol	Sorbitol	Formic acid	Ethylene glycol (EG)	Propylene glycol (PG)
Blank (no catalyst)	96	22.5	9.2	2.9	4.0	6.2	3.1
CNT	97	25.5	11.8	2.6	3.0	5.1	3.3
Ru/CNT	100	2.5	45.4	5.9	3.9	6.4	4.7

*Reaction conditions: xylan (0.75 g), water (300 mL), CNT or 0.4%Ru/CNT (0.3 g), 205 °C, 50 bar H₂, 150 rpm.

conditions, some reducing sugar (22.5%) could be detected. Using CNT as catalyst, the amount of sugar alcohols detected was still very little but the amount of xylose slightly increased. When Ru/CNT was used as catalyst, the yield of xylitol increased greatly (to 45.4%) and almost no xylose could be detected (2.5%). Also, there was a slight increase in the amount of sorbitol, EG and PG. When the reaction was performed without catalyst or in the presence of CNT, the reaction mixture started to become yellowish and then turned dark brown with the increase of the reaction time (Figure 6), indicating further degradation of products and formation of humins². It has also been reported by Käldström et al. that the unstable sugars degrade (caramelize) under high temperatures²⁹. At the end of the reaction, part of the humins formed was deposited on the stirrer and the wall of the reactor in both cases. Also, the 3-4% difference from 100% in the conversion of xylan (see Table 3) could probably be attributed to the formation of the solid product. On the opposite, in the presence of the metallic phase (Ru), the resulting mixture was transparent (Figure 6). As reported in the literature, xylose can be converted to furfural, which gives humins by polymerization^{1,2,23}. Therefore, the presence of the metallic phase is very important to assure the rapid hydrogenation of xylose to xylitol, suppressing the formation of furfural and subsequent polymerization to humins. These results indicate that the first step of conversion of xylan, which is the hydrolysis to xylose, can be carried out even under the conditions of the blank test and can be slightly enhanced by the presence of CNT. On the other hand, the second step - hydrogenation of xylose to xylitol, can only occur in the presence of the metallic phase (Ru).



Figure 6. Evolution of the reaction mixture colour with the reaction time with (CNT or Ru/CNT) or without (blank) catalyst.

In order to confirm this two-step process, the individual hydrolysis of xylan and hydrogenation of xylose were also tested. First, the

hydrolysis of xylan was carried out with CNT as catalyst and the main product observed was xylose with a yield of 42.3% (Figure 7). Also, a low amount of sugar alcohols was detected (xylitol). When the reaction was started using xylose as substrate (hydrogenation step) and Ru/CNT as catalyst, xylitol was produced with about 33.7% yield, which is close to that of the one-pot process with Ru/CNT as catalyst and xylan as starting material (45.4%). Moreover, the hydrogenation step was also performed using CNT as catalyst and both conversion of xylose (77.8%) and vield of xylitol (10.5%) were much lower indicating that the presence of the metallic phase is essential for the selective conversion of xylose to xylitol. So, these results confirm that the direct conversion of xylan to xylitol is in fact a two-step reaction where CNT promotes the hydrolysis of xylan to xylose and Ru catalyses its consecutive hydrogenation to xylitol. These results are in agreement with those obtained by Kusema et al. for the hydrolytic hydrogenation of arabinogalactan, where Ru demonstrated a high catalytic activity in the hydrogenation of arabinose and galactose, manifested by the high selectivity towards the corresponding polyols (arabitol and galactitol)¹¹. Accordingly, the reductive atmosphere (H_2) combined with the metallic phase of the catalyst, seems to be a good strategy to increase the selectivity of the reaction towards the more stable sugar alcohols.



Figure 7. Conversion of xylan (or xylose in the case of hydrogenation) and distribution of products after 30 min of reaction at different stages of the process. One-pot conditions: xylan (0.75 g), water (300 mL), 0.4%Ru/CNT (0.3 g), 205 °C, 50 bar H₂, 150 rpm. Hydrolysis conditions: xylan (0.75 g), water (300 mL), CNT (0.3 g), 205 °C, 3 bar N₂, 150 rpm. Hydrogenation conditions: xylose (0.75 g), water (300 mL), CNT or 0.4%Ru/CNT (0.3 g), 205 °C, 50 bar H₂, 150 rpm.

Effect of cellulose on the yield of xylitol produced from xylan.

Another set of experiments was performed using a mixture of xylan and cellulose as substrate, in order to evaluate the evolution of the

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conversion of both materials and the product distribution, as well as the effect that the presence of one material could have on the conversion of the other, taking into account that they are usually found combined in nature. For these experiments, 750 mg of cellulose, 750 mg of corncob xylan and 300 mg of catalyst (Ru/CNT) were added to 300 mL of water and introduced into the reactor. The reaction was carried out according to the standard conditions described in the Catalytic experiments section for the hydrolytic hydrogenation of corncob xylan. Also, two forms of cellulose were used: commercial microcrystalline cellulose (MC-cellulose) and ballmilled cellulose (BM-cellulose).

As aforementioned, xylitol and sorbitol are some of the most interesting products to be directly obtained from xylan and cellulose. Therefore, concerning this set of experiments, the formation of these two main products (sorbitol and xylitol) was evaluated. Besides sorbitol and xylitol, glucose, xylose, formic acid, EG and PG were also detected in very small amounts.



Figure 8. Evolution of the yields of xylitol (a) and sorbitol (b) during the one-pot conversion of xylan, cellulose and xylan+cellulose. Reaction conditions: xylan (0.75 g) and/or cellulose (0.75 g), water (300 mL), 0.4%Ru/CNT (0.3 g), 205 °C, 50 bar H₂, 150 rpm. For "1/2Xylan+1/2BM-cellulose+Ru/CNT" 0.375 g of each xylan and ball-milled cellulose was used instead of 0.75 g.

Performing the simultaneous hydrolytic hydrogenation of xylan and BM-cellulose, there was an enhancement in the production of the main products. In this case, yields of 48.3% of xylitol and 76.6% of sorbitol were reached in just 3 h of reaction (Figure 8),

corresponding to xylan and BM-cellulose conversions of 100 and 96.1%, respectively. So, an enhancement around 15 and 25% was observed in the yields of xylitol and sorbitol, respectively, in comparison to those observed when separately performing the conversion of xylan (34.2% yield of xylitol after 3 h) and BMcellulose (50.7% yield of sorbitol after 3 h). To check if the reason was the decrease of the catalyst/substrate ratio, another test was performed using half of the amount of substrate (375 mg of xylan and 375 mg of BM-cellulose) for the same amount of catalyst (300 mg) (reaction denoted as 1/2Xylan+1/2BM-cellulose+Ru/CNT in Figure 8), in order to maintain the initial substrate/catalyst ratio. Xylitol and sorbitol yields of 46.1 and 71.9% were achieved after 3 h, respectively, indicating that the enhanced yield is not due to the substrate/catalyst ratio, but results from a synergetic effect between the two substrates. Furthermore, this result shows that the amount of substrate can even be reduced, since the yields of xylitol and sorbitol obtained using 375 mg of each substrate are only slightly lower than those reached when using 750 mg of each substrate for the same amount of catalyst. Also, if MC-cellulose was converted simultaneously with xylan (instead of BM-cellulose), an enhancement in the yield of sorbitol from 8.7 to 26.7% after 3 h of reaction could be observed. On the other hand, the yield of xylitol was practically the same as that reached when simultaneously converting BM-cellulose and xylan, indicating that there is no effect of ball-milling of cellulose on the yield of xylitol, but its presence is sufficient. Note that practically no xylitol was observed for the conversion of cellulose (microcrystalline or ball-milled) (Figure 8a), as well as practically no sorbitol was observed during the conversion of xylan (Figure 8b).

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Figure 9. Effect of ball-milling cellulose together with the catalyst on the yields of xylitol (a) and sorbitol (b). Reaction conditions: xylan (0.75 g), cellulose (0.75 g), water (300 mL), 0.4%Ru/CNT catalyst (0.3 g), 205 °C, 50 bar H₂, 150 rpm.

In a previous work of our group²⁶, an enhanced yield of sorbitol (close to 70%) was attained by ball-milling cellulose together with the catalyst (Ru/AC) before performing the reaction at the same conditions as those used in the present work. That result was one of the best ever achieved for the one-pot conversion of cellulose by an environmentally friendly approach. Accordingly, in order to try to outperform that result, a new experiment was carried out, where the simultaneous conversion of xylan and cellulose ball-milled together with the catalyst (sample (Cellulose+Ru/CNT)_mix) was performed. As depicted in Figure 9, besides the enhanced yield of sorbitol (81.1% after 2 h), yields of xylitol around 60% were achieved in less than 1 h of reaction, with 100% conversion of both xylan and cellulose, making these results even more outstanding in both fields of direct and environmentally friendly conversion of hemicellulose (xylan) and cellulose.

Furthermore, recycling tests of the xylan and cellulose mixture were performed in order to evaluate the catalyst stability. For these tests, the catalyst was separated from the reaction mixture by filtration, washed with water and dried in an oven overnight. The recovered catalyst was then used in successive tests and the results are presented in Figure 10. No significant changes in yields of products were observed, indicating that the catalyst can be reused at least up to three cycles without metal leaching into solution and without loss in activity and selectivity.



Figure 10. Recycling tests of 0.4%Ru/CNT on the yield of xylitol and sorbitol after 5 h of reaction. Reaction conditions: xylan (0.75 g), ball-milled cellulose (0.75 g), water (300 mL), 0.4%Ru/CNT (0.3 g), 205 $^{\circ}$ C, 50 bar H₂, 150 rpm.

Although the comparison between the results obtained and those reported in literature can be particularly difficult due to the different conditions used from author to author, to the best of our knowledge, this is one of the best sorbitol and xylitol yields ever reported for the direct catalytic conversion of cellulose and hemicellulose by using an environmentally friendly approach.

Experimental

Chemicals and materials.

Hemicellulose (corncob xylan) was purchased from Carbosynth (min 95%). Microcrystalline cellulose, sorbitol (98%), xylitol (99%) and the metal precursor ruthenium (III) chloride (RuCl₃ 99.9%, Ru 38%) were supplied by Alfa Aesar. Nanocyl-3100 multi-walled carbon nanotubes were provided by Nanocyl. Xylose (99%) and glucose (99.5%) were supplied by Acros and Sigma, respectively. Sulphuric acid (> 95%) was obtained from Fisher Chemical. All solutions were prepared in ultrapure water with a conductivity of 18.2 μ S·cm⁻¹ obtained in a Milli-Q Millipore System.

Materials preparation.

A ruthenium catalyst (nominal metal loading of 0.4 wt%) was prepared by the incipient wetness impregnation method of commercial multi-walled carbon nanotubes (CNT) with an aqueous solution of the metallic precursor (RuCl₃). After impregnation, the resulting material was dried overnight in an oven at 110 °C. After thermal treatment under N₂ flow for 3 h, the catalyst was reduced under H₂ flow for 3 h. The appropriate reduction temperature (250 °C) was determined by TPR (see the Characterization of materials section) and the thermal treatment was carried out at the same temperature used for the reduction. The catalyst was denoted as Ru/CNT.

Hemicellulose (corncob xylan) was used as received, without any pre-treatment.

Microcrystalline cellulose (MC-cellulose) was ball-milled in a ceramic pot using a Retsch Mixer Mill MM200 apparatus operating at a frequency of 20 Hz for 4 h (see details in Ribeiro et al.²⁶), and denoted as BM-cellulose. MC-cellulose was also ball-milled together with the catalyst under the same conditions (denoted as mix-milling), and the sample was denoted as (Cellulose+Ru/CNT)_mix.

Materials characterization.

Both support and catalyst were characterized by N₂ 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 areas were calculated using the Brunauer-Emmett-Teller (BET) equation; micropore volumes (V_{micro}) and mesopore surface areas (S_{meso}) were obtained by the t-method. The TPR profile of the catalyst was obtained in a fully automated AMI-200 equipment (Altamira Instruments).

Microcrystalline cellulose and hemicellulose were characterized by elemental analysis and thermogravimetry (TG). Elemental analysis was performed on an EA1108 CHNS-O elemental analyser from Carlo Erba Instruments. TG analysis was carried out on a STA 409 PC/4/H Luxx Netzsch thermal analyser, where the samples were heated from 50 to 800 °C (heating rate of 10 °C·min⁻¹) under nitrogen or air.

Catalytic experiments.

The hydrolytic hydrogenation of hemicellulose (corncob xylan) was performed in a 1000 mL stainless steel Parr reactor. In standard tests, 300 mL of water, 750 mg of xylan and 300 mg of catalyst were introduced into the reactor under stirring at 150 rpm. After heating under nitrogen to the desired temperature (205 °C), the reaction

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was initiated by pressuring with hydrogen (50 bar) and stopped after 5 h. Samples (1 mL) were periodically withdrawn for analysis. In a typical hydrogenation experiment, xylose was used as substrate instead of xylan and the reaction was stopped after 1 h.

In a typical hydrolysis experiment, the system was not pressurized with hydrogen but kept under nitrogen atmosphere. The reaction was initiated when the desired temperature was achieved (205 °C) and stopped after 5 h.

Product analysis.

The reaction samples were analysed by high performance liquid chromatography (HPLC) using an Alltech OA-1000 ion exclusion column and a refractive index (RI) detector. H_2SO_4 (0.005 mol·L⁻¹) was used as eluent at a 0.5 mL·min⁻¹ flow rate and a volume of injection of 30 µL was selected. In some cases, an Alltech Prevail Carbohydrate ES 5 μ (250 mm × 4.6 mm) was used with acetonitrile:water (85:15) as eluent at a 1.4 mL·min⁻¹ flow rate and a volume of injection of 30 µL. Standards of xylan, xylose, glucose, xylitol, sorbitol, glycerol, EG, PG and formic acid were injected prior to reaction, and the respective calibration curves were drawn. The yield (Y_i) of each product *i* was determined as the ratio of the number of moles of product formed (measured by HPLC) to the total number of moles of substrate initially present. Cellulose and hemicellulose are mainly polymers of glucose and xylose units, respectively. The percentage of other components in cellulose or hemicellulose is not more than 15%¹², so for simplicity of calculations we considered that the conversion of cellulose is practically only into glucose and hemicellulose (xylan) into xylose.

The conversions of corncob xylan, xylose and glucose were calculated using equations (1), (2) and (3), respectively:

$$X_{xylan}(\%) = \frac{\text{moles}(Xylan_0) - \text{moles}(Xylan_f)}{\text{moles}(Xylan_0)} \times 100\% \quad (1)$$

$$X_{xylose}(\%) = \frac{\text{moles}(Xylose_0) - \text{moles}(Xylose_f)}{\text{moles}(Xylose_0)} \times 100\% \quad (2)$$

$$X_{glucose}(\%) = \frac{\text{moles}(\text{Glucose}_0) - \text{moles}(\text{Glucose}_f)}{\text{moles}(\text{Glucose}_0)} \times 100\%$$
(3)

The conversion of cellulose was determined based on the total organic carbon (TOC) data obtained with a Shimadzu TOC 5000-A according to equation (4):

X_{cellulose}(%) =

= moles of total organic carbon in the resultant liquid moles of carbon in cellulose charged into the reactor ×100% (4)

Conclusions

A carbon nanotubes supported ruthenium catalyst was tested on the one-pot conversion of corncob xylan to xylitol. The catalyst showed to be highly efficient and a yield of xylitol close to 50% was achieved in less than 1 h of reaction. Recycling experiments confirmed that the catalyst was stable during reaction and could be reused up to at least four successive runs without practically no loss in activity and selectivity. Hydrolysis of xylan and hydrogenation of xylose indicated that the hydrolysis to xylose can be performed even without catalyst at elevated temperature and that the metallic phase (Ru) is essential for the selective hydrogenation to xylitol.

Xylan was also converted simultaneously with cellulose, which allowed increasing the yields of xylitol and sorbitol in comparison to those achieved during the separate conversion of xylan and cellulose. As a result, yields of 48% of xylitol and 77% of sorbitol were reached in just 3 h of reaction, corresponding to an increase of the yields around 15 and 25%, respectively. If the cellulose was previously ball-milled together with the catalyst and then simultaneously converted with xylan, the yields of xylitol and sorbitol could be even further increased to 57 and 81%, respectively.

To the best of our knowledge, this article presents one of the best results ever attained for the direct catalytic conversion of xylan and cellulose into xylitol and sorbitol using an environmentally friendly process.

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