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Screening of catalysts and reaction conditions for the direct conversion of corncob xylan to xylitol

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Abstract: Different supported metal catalysts were tested for the one-pot transformation of corncob xylan to xylitol. The influence of several factors, such as catalytic support, nature of metal, metal loading, amount of catalyst, hydrogen pressure and reaction temperature, was investigated. The results revealed that xylan can be converted into xylitol with a yield close to 80% after 2 h of reaction using Ru supported on carbon nanotubes (CNT, 0.4 wt% metal loading) with excellent stability after repeated use, at a temperature of 170°C and an H2 pressure of 50 bar. The yield of xylitol achieved is one of the highest ever reported for the direct conversion of xylan to xylitol using an environmentally friendly process.

Keywords: corncob xylan; hydrolytic hydrogenation; Ru catalysts; xylitol.

1 Introduction

The continuous reduction of fossil resources urges modern society to implement alternative energy and valuable chemical resources [1]. Biomass has been pointed out as one of the most promising alternatives [2], being considered as the only sustainable source of organic carbon on earth and the perfect equivalent to petroleum for fuels and fine chemicals production with net zero carbon emission [1, 3]. Lignocellulose is an abundant feedstock that is not human digestible, so does not compete directly with food production, and is available as residue of forestry and agriculture or as waste from paper industry, making it a highly promising alternative to replace fossil fuel materials [4–6]. Lignocellulosic biomass essentially consists of cellulose, hemicelluloses and lignin [7, 8]. Hemicelluloses are the second most abundant polymer in biomass [1, 4]. Unlike cellulose, hemicelluloses have a random, branched and amorphous structure, which is composed of several heteropolymers including xylan, arabininoxylan, glucuronoxylan, galactomannan, glucomannan and xyloglucan [1, 9, 10]. Therefore, and in contrast to cellulose, the amorphous structure of hemicellulose allows it to exhibit higher reactivity for hydrolysis [4, 9].

There are various routes for converting hemicelluloses, such as pyrolysis to bio-oil, hydrolytic hydrogenation to polyols and hydrolysis to monomers. For the hydrolysis of hemicelluloses, several mineral acids (sulfuric, phosphoric, nitric and hydrochloric acids) and organic acids (trifluoroacetic, oxalic and acetic acids) are used and their performances are extensively described in published papers and reviews [11–13]. Heterogeneous catalysts such as zeolites, carbons, metal oxides, etc., well known in cellulose hydrolysis [14–19], have also been used for the hydrolysis of hemicelluloses [20, 21]. From the various heteropolymers of hemicelluloses, hydrolysis of xylans is one of the most studied systems due to the high availability of these polysaccharides from herbaceous plants and hardwoods [4, 13, 22, 23].

Much interest is being put on the one-pot catalytic transformation of cellulose and hemicelluloses using heterogeneous catalysts in aqueous media [5, 24–26]. The conversion of hemicelluloses, such as arabinoxylan and xylan, into polyols over various catalysts and supported metals has already been reported by Dhepe and Sahu [5], who investigated a one-pot process for the conversion of solid hemicellulose in aqueous media using solid Bronsted acid catalysts, and achieved the highest yields of arabinose and xylose with a HUSY zeolite. Kusema et al. [27] demonstrated selective hydrolysis of arabinogalactan over heterogeneous catalysts, and later Kusema et al. [28] and Murzin et al. [29] investigated the hydrolytic hydrogenation of arabinogalactan to galactitol and arabinitol over Ru-modified MCM-48 and HUSY zeolites, respectively. Yi and Zhang [30] tested the one-pot conversion of beechwood xylan to xylitol by transfer hydrogenation in isopropanol. The conversion of xylan to xylitol has also been reported with yields between 50% and 80% by using Ru/C...
2.2 Preparation of materials

Nanocyl-3100 multi-walled CNT were used as support for this study. An Ru catalyst was prepared by incipient wetness impregnation of CNT with a solution of the corresponding metallic precursor (RuCl₃). The amount of noble metal was calculated to achieve a metal loading of 0.4% wt. 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 was determined by temperature programmed reduction (TPR) (see Section 3.1.1), and the thermal treatment was carried out at the same temperature. The catalyst was denoted as 0.4%Ru/CNT.

Following this procedure, two series of CNT supported catalysts were prepared, one with different metal loadings (0.2 wt%, 0.4 wt%, 0.8 wt% and 1.2 wt% Ru) and the other with different metals (0.4%Ru/CNT, 0.4%Pt/CNT, 0.4%Pd/CNT, 0.4%Rh/CNT, 0.4%Ni/CNT).

Furthermore, another series of ruthenium catalysts was prepared with different catalytic supports. AC, graphite (GIT) and zeolite (HY) were used as supports and the different catalysts were denoted as 0.4%Ru/AC, 0.4%Ru/GIT and 0.4%Ru/HY.

HY zeolite was prepared by treating the commercial zeolite (Linde LZY62) under air flow for 8 h at 500°C.

2.3 Characterization of supports and catalysts

TPR profiles were obtained using fully automated AMI-200 equipment (Altamira Instruments). N₂ adsorption isotherms measured at −196°C were determined in a NOVA Quantachrome Instruments apparatus; surface areas were calculated using the Brunauer-Emmett-Teller (BET) equation. Further details can be found elsewhere [35].

2.4 Hydrolytic hydrogenation of xylan

In a standard experiment, 750 mg of corn cob xylan, 300 mg of catalyst and 300 ml of water were placed inside the reactor (1000 ml stainless steel Parr reactor). The reactor was then flushed with nitrogen to remove the air, pressurized with 4 bar of nitrogen and then pre-heated up to the desired temperature (205°C) under stirring at 150 rpm. When the desired temperature was achieved, pure hydrogen was introduced to obtain a total pressure of 50 bar inside the reactor and the reaction was initiated and kept for 2 h.

Samples periodically withdrawn from the reactor were analyzed by high performance liquid chromatography with a HITACHI Elite LaChrom equipped with a refractive index detector. An ion exclusion Alltech OA1000 column (300 mm × 6.5 mm) with a sulfuric acid solution (0.005 mol·l⁻¹) at a flow rate of 0.5 ml·min⁻¹ (as mobile phase) was used. In some cases, an Alltech Prevail Carbohydrate ES 5 μ (250 mm × 4.6 mm) was used with acetonitrile : water (85:15) at
1.4 ml·min⁻¹ as eluent and a volume of injection of 30 μl. Xylose, xylitol, sorbitol, formic acid, ethylene glycol and propylene glycol were the reaction products detected, in addition to other products that could not be identified. Since the main goal of this work was the optimization of the conditions for the direct conversion of xylan to xylitol, and because the other products detected presented yields lower than 10% under the conditions tested, the present work is focused on the production of xylitol. The yield of xylitol was determined as the ratio of the number of moles of xylitol formed to the total initial number of moles of xylan. Further details can be found elsewhere [36, 37].

The influence of the experimental conditions was investigated by varying the reaction temperature between 140°C and 215°C and the hydrogen pressure between 30 bar and 60 bar. The amount of catalyst was also varied between 150 mg and 750 mg, as well as the Ru loading from 0.2 to 1.2 wt%. Furthermore, the effect of the catalytic support and of the metal nature were also studied by using CNT, AC, GIT and HY as supports, and Ru, Rh, Pt, Pd and Ni as metals.

### 3 Results and discussion

#### 3.1 Characterizations

##### 3.1.1 TPR

The reduction ranges of the metal catalysts supported on CNT are shown in Figure 2. Ni catalyst shows a reduction peak around 380–450°C, while Pd catalyst presents a reduction range around 180–250°C. Pt and Rh catalysts present wide reduction peaks around 180–280°C and 100–250°C, respectively. The 0.4%Ru/CNT profile shows a reduction peak around 200–300°C. The reduction range of Ru remained practically unchanged with the variation of the metal loading (Figure 2B). TPR profiles of Ru supported on other materials can be found elsewhere [37]. According to these results, in order to assure effective reduction of the metal, Ni catalyst was reduced at 500°C for 3 h, whereas the remaining catalysts were reduced at 250°C for 3 h.

##### 3.1.2 N₂ adsorption

The original CNT sample shows an N₂ adsorption isotherm typical of non-microporous materials (Figure 3A). The textural properties of the Ru/CNT catalysts, namely the BET surface area, are not significantly different from those of the original support (Table 1). The results show a slight decrease of BET surface area after the impregnation with the metal phase and the increase in metal loading. Moreover, no significant difference was found in the BET surface area of the different metal catalysts (Figure 3B and Table 1). Therefore, it was assumed that the textural properties of the supported metal catalysts are not significantly different from those of the original support. Textural properties of Ru supported on other materials can be found elsewhere [37].

#### 3.2 Catalytic conversion of xylan

##### 3.2.1 Catalyst optimization

The selective conversion of corn cob xylan to xylitol was studied under the aforementioned standard conditions (see Section 2.4). The catalyst parameters (support, metal nature, metal loading and amount of catalyst) were investigated and optimized. In all tests, conversions of xylan of 100% were achieved in < 10 min.

We started to compare the catalytic performance of the catalysts supported on different materials. Figure 4 shows the yield of xylitol from xylan after 2 h of reaction over ruthenium catalysts supported on carbon materials (CNT, AC and GIT) and a zeolite (HY). A metal loading of 0.4% wt of Ru was selected in each case. Among the catalysts tested, 0.4%Ru/CNT presented the highest yield of xylitol (39%), which could be related to the highest dispersion of Ru on CNT (74%) comparatively to AC (66%), GIT (51%) and HY (61%) (see additional information in [37]).
Also, the measurement of the Ru nanoparticles allowed observation of narrow particle size distributions for Ru/CNT, Ru/AC and Ru/HY (from 0.5 to 2 nm), with average diameters of 1.0 nm, 1.4 nm and 1.6 nm, respectively, while Ru/GIT presented a wider particle size distribution, with an average diameter of 1.9 nm [37]. In a previous work, we compared the performance of these catalysts in the one-pot conversion of cellulose to sorbitol under the same conditions. In addition to CNT, AC, GIT and HY, other supports were also investigated, such as carbon xerogels, graphene, carbon black P80 and alumina [37]. We tried to find a relationship between the activity/selectivity and the properties of the supports (porosity, specific area, acidity) (see additional information in [37]), but no particular relationship was obtained from that study. In the present work, we only tested four different supports, so it is even harder to relate the results obtained to the textural properties of the supports. As result, CNT was the most efficient support for the direct transformation of xylan into xylitol. It is important to note that CNT supported Ru catalysts have also been reported in other works as the most effective for the conversion of cellulose under similar conditions [37, 38].

According to these results, the following studies were performed using CNT as catalytic support. Different metals (Pt, Pd, Rh and Ni) were loaded on CNT and tested on the reaction. Compared to Pd, Rh and Ni, CNT supported Pt was slightly more effective for the formation of xylitol, but 0.4%Ru/CNT exhibited the highest yield of xylitol among all the catalysts tested (Figure 5). Other investigation groups have also concluded that Ru and Pt catalyst were the most effective for the direct conversion of cellulose to sugar alcohols [38–41].

Therefore, since Ru supported on CNT showed the best results so far, the Ru loading was also varied in order to be optimized. As depicted in Figure 6, by increasing the Ru loading from 0.2 wt% to 0.4 wt%, an important increase in the yield of xylitol after 2 h of reaction was observed. However, further increase of the metal loading to 0.8 wt% and 1.2 wt% led to a decrease on the yield of xylitol, the maximum yield being attained over 0.4%Ru/CNT, which could be due to a better Ru dispersion on the support.
for this catalyst. At higher metal loadings, many other products (mostly unknown) were observed, which could be due to further degradation/isomerization of xylitol. Within the metal loading range studied in this work, the yields of xylitol were very different, indicating that the Ru loading has an important effect on the selective one-pot conversion of xylan to xylitol.

Finally, using an Ru loading of 0.4 wt%, the amount of catalyst was varied between 150 mg and 750 mg, under the same reaction conditions. Figure 7 shows that the yield of xylitol achieves a maximum (39%) when using 300 mg of catalyst (0.4%Ru/CNT). The reason may be that a greater catalyst amount facilitated both xylitol production and degradation, as well as other side reactions, as already observed by Zhang et al. [42]. Accordingly, this amount of catalyst was selected and used for further studies.

### 3.2.2 Reaction conditions

After optimization of the catalyst parameters, the reaction conditions such as pressure and temperature were also studied using 300 mg of 0.4%Ru/CNT as catalyst. Once more, conversions of xylan of 100% were attained in <10 min in all tests. The influence of the initial concentration of xylan was not studied since in a previous work we had already studied the effect of the concentration of cellulose in its direct conversion to sorbitol by varying the amount of cellulose loaded to the reactor from 300 mg to 3000 mg. The conversions obtained were practically the same and the selectivity to sorbitol reached a maximum for 750 mg, so we selected this amount for the respective studies [35–37] and used the same amount of xylan for comparative purposes.

The hydrogen pressure was varied between 30 bar and 60 bar and the evolution of the yield of xylitol with the reaction time is presented in Figure 8. An increase in the yield of xylitol is observed with the increase of the H₂ pressure until 50 bar, maintaining approximately constant at higher pressure. At 60 bar, the evolution of the xylitol yield does not vary significantly compared with that performed at 50 bar, so 50 bar was considered the optimum hydrogen pressure for this reaction.

To conclude, the effect of the reaction temperature was also investigated between 140°C and 215°C (Figure 9). The yield of xylitol increased greatly with the increase of the reaction temperature from 140°C to 170°C. Then, the yield of xylitol over 1 h of reaction slightly decreased with further increase of temperature to 190°C, decreasing even more at higher temperatures. These results agree with the literature, which indicates 140–190°C as the optimum range for the transformation of hemicelluloses to sugars [11]. The behavior observed for the variation of the yield of xylitol with the increase of temperature is similar to that reported by Yi and Zhang [30]. This occurs because,
if the reaction temperature is too high, the produced sugar alcohols (like xylitol) can be further transformed into undesirable by-products. The maximum yield of xylitol was achieved at 170°C. So, if the reaction temperature is decreased from the previously used 205°C–170°C, the yield of our main product (xylitol) can be greatly enhanced from 39% to 76%. This yield of xylitol is considerably high, also indicating that 0.4%Ru/CNT is a very active catalyst for the direct conversion of xylan to xylitol in water. Thus, considering the energy consumption and the yield of xylitol, the optimum temperature for the direct and selective conversion of xylan to xylitol is 170°C. To the best of our knowledge, this is one of the highest yields of xylitol ever obtained directly from corncob xylan and by an environmentally friendly process.

Finally, in order to investigate the reproducibility of the catalytic tests and the errors associated to the conversion of xylan, four experiments with different samples of the 0.4%Ru/CNT catalyst were carried out. The maximum relative error observed was ±3% for the conversion and ±0.8% for the xylitol yield. Furthermore, in order to evaluate the catalyst stability, recycling tests were performed by recovering the catalyst from the reaction mixture by filtration and using it without any treatment in successive tests, after appropriate washing and drying. 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. As can be observed in Figure 10, the catalyst was stable during reaction at 170°C and could be reused up to at least four successive runs with practically no loss in activity and selectivity or metal leaching to solution. Also, no insoluble solid depositions on the surface of the catalyst, or changes of the textural catalytic properties were observed at least up to the fourth run. The same had been previously observed when converting xylan at 205°C using the same catalyst and experimental conditions [36]. Although Ru is a high-priced metal, the loading of metal used in this work was very low (0.4 wt%) and the catalyst was shown to be recyclable. Therefore, since the yield of xylitol achieved in this work is close to 80%, its high value would compensate the use of a high-priced metal such as Ru, once other less expensive metals also studied (e.g. Ni) are not efficient for the conversion of xylan to xylitol.

4 Conclusions

Several catalysts, with different supports, metals and metal loadings, were examined as catalysts for the hydrolytic hydrogenation of corncob xylan. Ruthenium supported on CNT was shown to be the most efficient catalyst
for the direct conversion of xylan to xylitol in water media. After an appropriate selection of catalyst and reaction conditions, a xylitol yield close to 80% could be attained after 2 h of reaction using Ru/CNT with 0.4 wt% of metal, at 170°C and 50 bar of H₂. In addition, the catalyst showed excellent stability at least up to four successive cycles. To the best of our knowledge, this work presents one of the best results ever achieved for the direct conversion of xylan into xylitol using a green process.

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References

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