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Exploring the reaction conditions for Ru/C catalyzed selective hydrogenolysis of xylitol alkaline aqueous solutions to glycols in a trickle-bed reactor

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ABSTRACT

The hydrogenolysis of an alkaline aqueous solution of xylitol to mainly ethylene- and propylene-glycols was studied over a Ru/C catalyst in a high pressure fixed-bed reactor run in the trickle-bed mode with cocurrent downflow of liquid feed and hydrogen. The effects of reaction parameters including H₂ pressure (40-80 bar), temperature (190-200 °C) and pH values (NaOH/xylitol molar ratio in the range 0.1-0.2, pH 9–12) and residence time have been explored to increase the selectivity of this reaction to the desired ethyleneglycol product. The activity and final products distribution were much influenced by the hydrogen pressure. An optimum to afford a high conversion and a high selectivity to ethyleneglycol at different space times was found at 60 bar. The effects observed are in agreement with the reaction pathways previously proposed and the relative reaction rates of the dehydrogenation/hydrogenation and base-catalyzed reactions of the intermediates are affected by the hydrogen pressure and the concentration of the alkaline promoter.

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1. Introduction

The substitution of fossil feedstocks by the abundant lignocellulosic biomass for the production of fuels and valuable chemicals has been receiving increased attention in recent years [1–6]. Non-edible cellulose and hemicelluloses can be depolymerized by controlled hydrolysis to several sugar monomers (glucose, xylose, arabinose, ...), which can then be catalytically hydrogenated into the corresponding sugar alcohols (sorbitol, xylitol, arabitol) [6–11]. Further catalytic hydrogenolysis of these polyols under alkaline aqueous conditions can then give access to glycols, such as ethylene glycol (EG), propylene glycol (1,2-PDO), and glycerol (GLY) [11–39]. EG and 1,2-PDO are widely used as monomers in polyester synthesis, as antifreeze or cooling fluids While previously the formation of glycerol was the main objective in the hydrogenolysis of polyols, nowadays, the interest has shifted towards EG and 1,2-PDO, the consumption of which is increasing. In particular, EG is

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used in large amounts as a monomer in the manufacture of biopolymers for drinking bottles. EG and 1,2-PDO are currently produced from petroleum-based ethylene and propylene via their epoxide [40]. Their demand is continuously increasing, and producing these glycols from renewable biomass could be a potential competitive or complementary process.

Hydrogenolysis of polyols to EG and 1,2-PDO has been described in patents as well as in academic publications. Hydrogenolysis of the C6 sugar alcohol sorbitol has received particular attention as early as in the years 1943–1958 [13–15] and in the last two decades [26-28]. Hydrogenolysis of glycerol (GLY) has been extensively studied in recent years [see reviews 2,6,12]. There are fewer studies on the hydrogenolysis of the C5 sugar alcohol xylitol [13,14,16,17,26,28,29,31,37,39]. However, xylose is the main component of hemicelluloses and is the second most abundant renewable sugar in nature, after glucose. It is a potentially cheap material, which will become largely available. Moreover, since xylose is more difficult to convert by fermentation to ethanol than glucose, alternative strategies of applications of xylose are envisaged. Xylitol produced by hydrogenation is thus an attractive alternative material for production of glycols which could also

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Scheme 1. Xylitol hydrogenolysis under alkaline conditions.

make the process of hydrogenolysis more economically interesting. In addition, xylitol hydrogenolysis is claimed to give possibly higher yield in EG than sorbitol [31,37].

Besides, let us mention some recent strategies to carry out the one-pot conversion of cellulose to the glycols by achieving simultaneous hydrolysis and hydrogenolysis, using multifunctional catalysts containing tungsten species [41–43].

A major challenge in polyol hydrogenolysis to glycols is to achieve a high selectivity to one or two desired products. The process involves cleavage of specific C–C and C–O bonds in the polyol chain; it is usually performed over supported metallic catalysts in the presence of inorganic hydroxide bases which enhance hydrogenolysis rates [21,24,25,30]. The temperatures used are in the range 180–250 °C and elevated H₂ pressures are used of 35–200 bar. Generally, very high pressures over Ni help to achieve a high selectivity in GLY [14]; preferred conditions on Ru are 220–270 °C and 75–150 bar, giving 1,2-PDO as the main product [27].

The mechanism proposed is a complex reaction pathway with a range of consecutive and parallel reactions including dehydrogenation, retro-aldol condensation, dehydration and hydrogenation reactions [14,22,23,39]. In this process the metallic component catalyses the hydrogenation/dehydrogenation reactions while the addition of a inorganic hydroxide base (sodium or calcium hydroxide) serves to the dehydration/retro-aldol reactions giving C—C and C—O scissions, in the initial polyol but also in the resulting intermediates.

More precisely, in the mechanism proposed (Scheme 1) [25,39], the reaction is initiated by reversible dehydrogenation of xylitol to xylose on the metallic function (even under high hydrogen pressure). Xylose under basic conditions can then undergo C—C bond cleavage through a retro-aldol reaction to form glycolaldehyde and glyceraldehyde; these aldehydic intermediates are further hydrogenated on the metal to form EG and GLY, respectively. Xylose can also undergo a C-O bond cleavage by dehydration. Alternatively, under basic conditions, glyceraldehyde is dehydrated to pyruvaldehyde and then transformed into 1,2-PDO or lactate. Similarly, retro-aldol reaction of glyceraldehyde leads to the formation of glycolaldehyde that is further hydrogenated to EG, and formaldehyde which can be transformed to formic acid FA via Cannizzaro reaction. Detailed examination of the product distribution during hydrogenolysis of different polyol stereoisomers over a Ru/C catalyst recently demonstrated that terminal C—C scission through decarbonylation could also be an important pathway to consider [40]; indeed, in this study, threitol was the only tetritol formed from xylitol while erythritol was only detected in ribitol hydrogenation. This product distribution and the absence of erythritol in xylitol hydrogenolysis would not result from a retro-aldol scission mechanism, and could only be explained by a terminal C—C scission.

The objective of this work was to examine the hydrogenolysis of C5 sugar alcohols produced from the hydrolysis of hemicelluloses. Before using actual hemicelluloses derived feedstock, we explored how the pressure (in the range 40-80 bar) in different base concentration conditions may control the product yield to a useful product, EG or 1,2-PDO, in the mixture of components of hydrogenolysis of xylitol as C5 model compound. So far, Ni, Ru, Pd, Pt, Rh, Ir have been employed, but ruthenium supported catalysts are usually more active and more stable than nickel catalysts for instance [21,33,38]. Further, among different ruthenium catalysts supported on solids of different basicities, Ru/C was found to be the more active and selective, with a lower formation of lactate, and it was shown to be stable after six recycling [21]. In this work, we evaluated a carbon-supported ruthenium catalyst in a continuous reactor in the hydrogenolysis of a synthetic solution of xylitol as the feedstock. Besides the problems of selectivity to the desired product, the stability of the catalyst was verified under these different operating conditions over periods up to 3 months.

2. Material and methods

2.1. Catalyst

The activated carbon supported catalyst 2 wt.%Ru/C was provided by Johnson Matthey (Extrudate type 642). The catalyst was handled as pellets of about 2 mm diameter and was used as such.

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2.2. Trickle-bed reactor

The hydrogenolysis reactions of aqueous solution of xylitol (200 gL^{-1}) were performed in a laboratory scale, high-pressure fixed-bed reactor run in the trickle-bed mode with co-current downflow of liquid feed and hydrogen. The system consisted of a tube made of Hastelloy C (1 cm inner diameter and 15 cm in length) that was heated by a tubular furnace. For each series of experiments, the tube was packed with the catalyst located in the isothermal portion of the reactor tube between two layers of inert packing material (1 mm spherical glass or low surface area titania particles) and two sintered stainless-steel filters at the inlet and exit of the reactor. The temperature of the catalytic bed was monitored and controlled via a thermocouple placed into a thermowell inserted in the reactor tube. The liquid feed, constituted of a xylitol aqueous solution with NaOH as basic promoter, was introduced from a feed glass tank into the system by an HPLC pump through the filter at the top of the column. The pressure and the flow rate of the gas were controlled with a back-pressure controller. The system was also equipped with a heat exchanger, a high-pressure gas-liquid separator from which the liquid effluent was continuously drained and collected in a flask with a liquid level control device and the gas stream discharged.

Initially, after purging with Ar, the catalyst was re-activated overnight under hydrogen gas flow at 200 °C under 40 bar. The temperature, the hydrogen pressure and flow, and a water flow, were set at the desired values. Upon entering the reactor, the aqueous solution and hydrogen were mixed and heated in the inert packing before contacting the catalyst. Once the system was stabilized at these reaction conditions, the water flow was replaced by a flow of the xylitol alkaline aqueous solution (10.2 mL h^{-1}) in the reservoir. The gas flow stream was fixed at 20 NL h⁻¹, giving in these experiments a high hydrogen to xylitol feed molar ratio > 60. Lower ratios of 5–7 were used on the pilot plant, which did not change significantly the selectivity. The solution was cooled in a condenser and the gas was vented. The liquid sample at the exit was collected and periodically withdrawn for off-line analysis.

2.3. Analytical procedures

The main products of the hydrogenolysis reaction of xylitol are EG, 1,2-PDO and GLY. Other hydrogenolysis products which may be formed are tetritols (threitol and erythritol), butanediols, light alcohols and some carboxylic acids. Reaction samples (dilution by a factor of 20-25 before HPLC analysis) were analyzed using a Shimadzu LC 20A HPLC connected to a RI detector and a UV detector at 210 nm, using a Transgenomic Coregel 107H column (L = 300 mm, Ø = 7.8 mm) heated at 65 °C. Elution was performed by 0.6 mLmin⁻¹ 0.01 N H₂SO₄ mobile phase. With such conditions, in addition of xylitol and xylose, the C4-polyols (butanediol isomers - BDOs, threitol, erythritol), C3-polyols (glycerol - GLY, 1,2-propanediol - 1,2-PDO), C2 polyol (ethyleneglycol - EG), C1-C3 alcohols (methanol, ethanol, 1- and 2-propanol), C1-C3-carboxylic acids (formic, acetic, lactic, propionic acids) could be analyzed. Calibration curves were established for the quantification of the products.

The Total Organic Carbon (TOC) of the solutions was measured, using a TOC-V_{CSH} analyzer, to check the material balance and the possible formation of gaseous products (methane, ethane) by cleavage in the experimental conditions used. A dilution factor of 400–500 of the samples was applied before the TOC analysis to be within the concentrations of the calibration curves, so that the results are obtained with $\pm 2 \text{ gL}^{-1}$. The pH of the solution was measured ex situ using a Meterlab PHM 240 pH-meter.

The results are expressed in terms of weight concentrations of xylitol converted and in the formed products, xylitol conversions,

and molar selectivities to the different products. The conversion is defined as the percentage ratio of the amount of xylitol converted to the amount of xylitol in the feed stream. The description of the results by weight concentrations has the advantage to show directly the production of products compared to the concentration of converted xylitol, without taking into account the differences in molecular weights of the different products. The selectivity to a particular product is defined as the percentage ratio of the molar concentration in this product to the total molar xylitol concentration converted, without accounting the number of carbons in the molecules. Therein, if one considers that one mole of xylitol will ideally yield one mol of EG and one mol of 1,2-PDO, the selectivity to each product should be then 100%. It gives an indication of the efficiency of the reaction in producing one desired product.

3. Results and discussion

Hydrogenolysis reactions of alkaline solutions of xylitol $(20 \text{ wt.\%}, 200 \text{ g L}^{-1})$ were conducted to investigate how the pressure in the range 40–80 bar in different concentrations of NaOH, influence xylitol conversion and product distribution. Two masses of catalysts were packed in the reactor in two separate series of experiments to examine the effect at different space times.

The temperature was chosen at 190–200 °C to minimize the possible formation of gaseous products on ruthenium. These temperatures were found appropriate and are close to those used recently for hydrogenolysis of sorbitol or xylitol over Ni-Re/C [29,31] or carbon-supported Ru catalysts [33,34,37] or Ni and Pt [35]. Sun et al. [37] observed that the activity and selectivity of Ru/C in the presence of Ca(OH)₂ as solid base depended largely on the H₂ pressure, temperature and amount of base in batch experiments and the selectivities were governed by the relative rates of the different competitive reactions.

3.1. Reaction at low conversion of xylitol

3.1.1. Effect of reaction conditions

Hydrogenolysis of a xylitol solution (20 wt.%, 200 g L^{-1}) was performed over an initial loading of a relatively low mass of 2 wt.%Ru/C catalyst (1.15 g, 7.5 cm height in the reactor in the isothermal part of the tube) between two layers of inert material. With a liquid flow rate of 10.2 mLh⁻¹, this corresponds to a space time of $1.13 g_{Ru} h g_{xylitol}^{-1}$. After purging with nitrogen, the reactor was heated to the desired temperature of 200 °C under H₂ flow rate of $20 \text{ NL} \text{ h}^{-1}$. The reaction was performed at two temperatures (190 °C and $200 \,^{\circ}\text{C}$) at different pressures (40-80 bar) and different base concentrations (0.13-0.26 M NaOH, corresponding to molar ratios of NaOH/xylitol of 0.1-0.2). Indeed, it has been shown that the reaction rate depends on the amount of base and that the selectivity to glycols can markedly be increased without decreasing polyol conversion when an inorganic hydroxide base is added [15,21,24,33]. The alkaline nature of the mixture produced from the hydrogenolysis is also helpful in the downstream section. Indeed, at that higher pH, the volatility of all the organic acids (acetic, formic, etc.) byproducts is lowered, thus it is easier to separate them from the light glycols (EG, PDO). Each condition was evaluated for at least 100 h to check the stability of the catalyst.

Fig. 1 shows the data while applying a sequence of different operating conditions. Due to the complex reaction network with several parallel and consecutive reactions, a wide product distribution was observed. It shows the concentration of xylitol converted and the bar cumulative weight concentrations of main polyols produced in the samples periodically taken at the outlet of the reactor: EG, 1,2-PDO, GLY, and butanediols (2,3-BDO + 1,3-BDO + 1,4-BDO) and formic acid FA. Threitol was also detected in small amounts but

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Fig. 1. Hydrogenolysis of xylitol (200 g L^{-1}) under various T, P, and pH conditions at space time of $1.13 \text{ gRu} \text{ hg}_{xylitol}^{-1}$. Concentration of converted xylitol (\bullet) versus bar cumulative concentrations of products analyzed in the different samples taken at the exit of the reactor: (from bottom to top: 1,2-PDO, EG, GLY, formic acid FA, BDO). Threitol was present but not quantified. step1 (time on stream 0 to 49 h): $T = 200 \,^{\circ}$ C, NaOH = 0.13 M, P = 40 bar; step 2 (49–145 h): $T = 200 \,^{\circ}$ C, NaOH = 0.20 M, P = 40 bar; step 3 (145–213 h): $T = 200 \,^{\circ}$ C, NaOH = 0.20 M, P = 60 bar; step 4: (213–337 h): $T = 200 \,^{\circ}$ C, NaOH = 0.20 M, P = 80 bar; step 5 (337–457 h): $T = 200 \,^{\circ}$ C, NaOH = 0.26 M, P = 80 bar; step 7 (553–717 h): $T = 190 \,^{\circ}$ C, NaOH = 0.26 M, P = 60 bar; step 8 (717–890 h): $T = 190 \,^{\circ}$ C, NaOH = 0.26 M, P = 80 bar; step 10 (1052–1193 h): same conditions as in step 2.



Fig. 2. Selectivity to (**I**) EG, (**A**) 1,2-PDO, (•) GLY, and (×) BDO during xylitol hydrogenolysis at space time 1.13 gRu $h g_{xylitol}^{-1}$ under various *T*, *P*, and pH conditions (see Fig. 1). Selectivity to FA was not represented for clarity of the figure.

could not quantified for this series of experiments, since using the analysis procedure adopted there was an overlap with an unidentified compound in very small amounts. Monoalcohols (MeOH, EtOH, ...) were, if detected, only in trace amounts. No isomerization of xylitol to arabitol was observed. Fig. 2 shows the selectivity to the main products versus time during this sequence.

Under these conditions and using this space time, xylitol conversion was in the range 20–34% corresponding to $40-68\,g\,L^{-1}$ concentrations of converted xylitol.

The reaction was started at 200 °C under 40 bar H_2 with a 0.13 M alkaline solution (NaOH/xylitol = 0.1) (step 1). Conversion was ca. 25% and the solution at the outlet was brown colored. The analysis demonstrated the presence of 1,2-PDO (11 g L⁻¹), EG (9.5 g L⁻¹), BDO (2.9 g L⁻¹), GLY (1.5 g L⁻¹) and FA (1.65 g L⁻¹).

After 50 h on stream, the concentration of NaOH was increased to 0.20 M (pH 9) while keeping the same temperature and pressure. The pressure was thereafter changed to 60 bar and finally 80 bar (steps 2–4). Conversion was 30% under 40 bar and it still improved slightly to 33% as the pressure was increased to 60 bar.

At the same time, concentrations in EG, 1,2-PDO and GLY increased significantly to attain 17.2, 15.3 and $3.9 \,\mathrm{g}\,\mathrm{L}^{-1}$, respectively (selectivity in EG, 1,2-PDO and GLY changed from 43%, 38% and 5% under 40 bar to 61%, 43% and 9% under 60 bar, respectively). However, upon applying a higher pressure of 80 bar, conversion dropped down to 25%; consequently, lower concentrations in the main products were observed ($13.1 \,\mathrm{g}\,\mathrm{L}^{-1}$ EG, $11.1 \,\mathrm{g}\,\mathrm{L}^{-1}$ 1,2-PDO and $3.5 \,\mathrm{g}\,\mathrm{L}^{-1}$ GLY). Interestingly, the highest pressure helped also to achieve a low concentration in butanediols which decreased from $3.6 \,\mathrm{g}\,\mathrm{L}^{-1}$ under 40 bar to $0.6 \,\mathrm{g}\,\mathrm{L}^{-1}$ under 80 bar. The concentration in formic acid was also the lowest at the highest pressure. As a consequence, the selectivity to the desired products increased significantly (60% EG and 41% 1,2-PDO). The liquid phase at the exit changed from brown to yellow and nearly colorless as pressure increased.

While keeping a temperature of 200°C, a higher NaOH concentration of 0.26 M (pH 12) slightly enhanced cleavage of xylitol when compared to the concentration of 0.20 M (steps 5 and 6 to compare with steps 3 and 4). This increased conversion is mainly due to the promoting effect of the base in the retro-aldol reaction of the xylose intermediate. The effect of the pressure under these new conditions (60 or 80 bar) was as observed when using 0.20 M NaOH aqueous solutions: conversion under 80 bar was lower than under 60 bar (29% instead of 34%). The concentrations of the different products decreased: EG and 1,2-PDO concentrations decreased from $18-20 \text{ g L}^{-1}$ and $16.5-19.5 \text{ g L}^{-1}$, respectively, to 15.9 g L^{-1} and 13.6 gL⁻¹, respectively; BDO concentration decreased from 2.6–3 g L^{-1} to 0.9 g L^{-1} and a smaller concentration of formic acid was formed under the higher pressure (2.0 instead of 2.6 g L^{-1}). The outlet liquid which was dark yellow under 60 bar became pale vellow under 80 bar.

The reaction was then conducted at 190 °C, and the pressure (40–80 bar) was again examined (steps 7–9). The same trends were observed: the conversion of xylitol decreased as pressure increased, EG concentration was the highest under 60 bar (15.4 g L⁻¹). 1,2-PDO, BDO and FA concentrations decreased and glycerol concentration increased. The liquid also became colorless under high H₂ pressure.

In the final step (step 10), the conditions of step 2 were again applied (0.20 M NaOH, $200 \degree \text{C}$, 40 bar). It was observed that the catalyst lost only ca.10% of its initial activity after 900 h on stream, and the concentrations in the produced compounds were not too different from those observed in step 2. This indicates that the catalyst maintained the initial selectivities to the different products, even if it had been slightly deactivated.

The data in Fig. 2 for selectivity, as defined in the experimental part, indicate that whatever the reaction conditions, the selectivity to 1,2-PDO did not change much and was in the range 35–45%, while selectivity to EG was more strongly influenced by the reaction conditions and varied in the range 43–66%. The best selectivity to EG was usually attained at 60 bar. The selectivity to BDO was strongly affected by the pressure; the highest the pressure, the lowest the concentration.

These results are further illustrated in Fig. 3a–c showing the evolution of average conversions and weight concentrations in the main products as a function of the pressure for the different NaOH concentrations and temperatures examined.

These results clearly evidence the existence of an optimum pressure for the catalytic system for xylitol conversion. This optimum at 60 bar can be explained if one considers the proposed reaction mechanism involving reversible dehydrogenation and hydrogenation reactions and requiring a good balance between these competing reactions. In the patent of Gubitosa and Casale [26], using Ru supported on activated carbon, it was claimed that the preferred reaction conditions for sorbitol, mannitol and xylitol hydrogenolysis to lower alcohols in the presence of BaOH were



Fig. 3. Average catalyst performances (conversion (\blacklozenge) and concentrations in the main products: (\blacksquare) EG, (\blacktriangle) 1,2-PDO, (\bullet) GLY, (\times) BDO, and (\bigcirc) FA) at each reaction conditions (a) 200 °C, 0.20 M NaOH (steps 2–4), (b) 200 °C, 0.26 M NaOH (steps 5 and 6), (c) 190 °C, 0.26 M NaOH (steps 7–9).

220–270 °C and 75–150 bar H_2 in a fixed-bed reactor. The preferred pressure under our conditions was found much lower.

Also, the influence on the productions of glycerol (which increased as pressure was increased) and BDO (which decreased as pressure was increased) is clearly observed (Fig. 2). The increase of GLY concentration with pressure is in agreement with previous studies whose aim was GLY which noted that high pressures help to achieve a high selectivity for GLY [14].

Considering the influence of NaOH concentration, it is clear that whatever the other reaction conditions, increasing concentrations of NaOH allowed an increase of xylitol conversion without significantly modifying selectivities to the different products.

Finally, the Total Organic Carbon (TOC) content of the different samples was measured using the Shimadzu TOC analyzer. The initial 20 wt.% xylitol solution contained ca. $80 \, g \, L^{-1}$ TOC and the TOC

threitol × BDO FA GLY 1,2-PDO = EG • xylitol converted threitol × BDO = xylitol conve

Fig. 4. Hydrogenolysis of xylitol (200 g/L in 0.26 M NaOH aqueous solution, T = 200 °C at space time = 2.08 gRu h g_{xylitol}⁻¹ liquid flow rate = 10.2 mLh⁻¹, H₂ gas flow = 20 NLh⁻¹, under various pressures. Concentration of converted xylitol (•) versus bar cumulative concentrations of products.

analysis showed that there was no significant loss of carbon material in the liquid phase in the different samples, which should not exceed a few percentages. Moreover, the TOC content was also calculated from the HPLC results and compared to the measured TOC values. This comparison showed that 90–95% of the carbon present in the outlet solution could be analyzed by HPLC, which is further consistent with the HPLC chromatograms which showed that the peaks which could not be quantified represented only a very low fraction of the total area.

3.1.2. Effect of xylitol concentration

Before the reaction was stopped, the reactor was fed with a less concentrated solution of xylitol $(50 \, g \, L^{-1})$ at time on stream 1200 h, while keeping the NaOH concentration at 0.26 M (NaOH/xylitol=0.8) and the same H₂ flow rate. Two pressures, 40 bar and 80 bar, were tested. Xylitol conversion increased to 80-90% under 40 bar and selectivity distribution was 32% to 1,2-PDO, 22% to EG, 9% to BDO and 3% to GLY. Under 80 bar, conversion decreased dramatically to 50%, the yields to glycols were much lower and selectivity was 25%, 25%, 5% and 9% to the previously mentioned products, respectively. These experiments suggest again that too high pressure or hydrogen flow have a negative impact on the reaction rate by slowing the initial reaction step of dehydrogenation which is a rate determining step.

3.1.3. Leaching of Ru catalyst

Different samples were analyzed by ICP-OES for possible leaching of the metallic phase. The samples at time on stream 117 h, 185 h, 313 h, 353 h, 525 h, 669 h, 793 h, 870 h, 1005 h, 1152 h, representative of the different operating conditions did not contain Ru over the detection limit of the method (<0.1 mg L⁻¹).

3.2. Effect of pressure at higher xylitol conversion

Experiments were also performed at higher xylitol conversion, by loading a new catalyst sample (2.2 g catalyst) in the reactor. The reaction was performed at 200 °C using a 20 wt.% xylitol solution in 0.26 M NaOH (NaOH/xylitol=0.2) and the same liquid feedstream flow rate (10.2 mL h^{-1}). The space time was then 2.08 g_{Ru} h g_{xylitol}⁻¹ which should achieve higher xylitol conversions. The effect of pressure was studied in the range 40–80 bar. The results are shown in Fig. 4 for the cumulative concentrations of main products vs concentration of xylitol converted, and in Fig. 5 for the selectivity as a function of time under the different conditions.

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Fig. 5. Selectivity to (**■**) EG, (**▲**) 1,2-PDO, (**•**) GLY, and (×) BDO during xylitol hydrogenolysis at space time 2.08 gRu h $g_{xylitol}^{-1}$ under various pressures. Selectivity to FA and threitol were not represented for clarity of the figure.

The HPLC analysis procedure was improved and threitol and erythrytol could be quantified in these experiments. However, no erythritol was detected, which is in accordance with the demonstration of Deutsch et al. [39] on the exclusive formation of threitol by terminal C—C scission from xylitol. The comparison of converted xylitol concentration and the cumulative concentrations of products analyzed shows that they match relatively well.

As one would expect, the increase of space time increased the conversion which was ca. 60% vs. ca. 30% in the previous set of experiments.

The reaction was started under 60 bar. Conversion of xylitol decreased slightly from 66% to 55% over the period of 286 h. However the yields in the different products changed little and the solution was colorless. EG was produced as the main glycol. The yields in EG, 1,2-PDO, GLY, BDO, formic acid and threitol were ca. 40 g L^{-1} , 35 g L^{-1} , 6.5 g L^{-1} , 4.5 g L^{-1} , 4 g L^{-1} , and 12 g L^{-1} , respectively. The selectivity to EG was high (75%) and higher than the selectivity to 1,2-PDO (57%).

By decreasing the pressure to 40 bar, conversion remained initially at the same level (55–50% conversion), then it decreased at a significant rate and was no more than 40% after 498 h on stream. The outlet solution was trouble and yellow-brown, and turned rapidly to dark brown when kept at ambient temperature. As a consequence, the yields in EG and 1,2-PDO decreased. However, selectivities were constant; they were ca. 56% to EG and 43% to 1,2-PDO, lower than under 60 bar. As observed at lower conversion, a lower pressure gave a lower yield in GLY which was nearly absent in the reaction mixture under these conditions. BDO concentration was also found to decrease (to ca. $2 g L^{-1}$), whereas threitol formation was found to increase ($15 g L^{-1}$).

Under 80 bar, hydrogen pressure was defavorable for the initial dehydrogenation reaction, and conversion was ca. 37%. However, it was stable over 100 h. Low yields in the desired products were observed, but the mass balance was good. Selectivity to EG (70%) was again higher than selectivity to 1,2-PDO (48%). GLY production was higher (7 g L⁻¹), since high hydrogen pressure has been shown to favor GLY formation. The data indicate little or no change in the product distribution as xylitol conversion increased. The high selectivity to EG (and 1,2-PDO) can be retained at higher conversion of xylitol.

In this set of experiments, the same effect of pressure was observed as at lower conversion, and an optimum pressure of 60 bar was determined for conversion.

As regarding variations of the selectivities at the optimum pressure of 60 bar as a function of conversion in the continuous reactor, both the selectivities to EG and 1,2-PDO were found to increase slightly with conversion from 61–66% and 43–47%, respectively, to 75% and 57%, respectively. On the other hand, selectivity to glycerol and BDO remained at the same value of 9–11% and 5–6%, respectively. Sun et al. [37] also examined the dependence of the selectivities as a function of xylitol conversion over Ru/C in the presence of Ca(OH)₂ at 200 °C under 40 bar. They noted that the selectivity to 1,2-PDO increased slightly and selectivity to EG remained essentially constant. However, a dramatic decrease in selectivity to GLY was observed to form lactic acid. In contrast to these results in batch reactor, selectivity to GLY in the continuous reactor did not vary, and lactate was not observed in measurable amounts. Since lactate is thought to be formed by the competitive dehydration of glyceraldehyde and base-catalyzed conversion (Scheme 1), this suggests that in the case of the continuous reactor, the feed of hydrogen is high enough so that glyceraldehyde will readily be hydrogenated to GLY over the Ru catalyst. This is further illustrated by the results of Sun et al., who observed an important formation of lactate under nitrogen and further a dramatic decrease in selectivity of lactate with increasing H₂ pressure from 0 to 40 bar [37].

3.3. Discussion on the effect of hydrogen pressure

Taken together, the results of xylitol hydrogenolysis in the continuous trickle-bed reactor indicate the existence of an optimum hydrogen pressure for xylitol conversion, which under our reaction conditions was situated at ca. 60 bar. Comparing 80 and 175 bar at pH 12.5 at 210 °C, an inhibiting effect for the conversion of sorbitol was observed over a Ru/SiO₂ catalyst [21]. Effects of variation of hydrogen pressure on conversion were also analyzed in the hydrogenolysis of xylitol over Ru/C in the presence of Ca(OH)₂ at 200 °C [37] or in the hydrogenolysis of sorbitol over a carbon nanofiber supported catalyst in the presence of at 220 °C [33] in batch experiments. The activity of Ru/C increased continuously with increasing pressure in the range 0-100 bar in xylitol hydrogenolysis [37]. In the hydrogenolysis of sorbitol in the range 60-100 bar, increased sorbitol conversion was obtained when increasing pressure from 60 bar to 80 bar, but further increase in the pressure slightly decreased conversion, giving a preferable hydrogen pressure of ca. 80 bar [33]. As in this previous work in batch reactor, the existence of an optimum pressure can be explained on the basis of the reaction mechanism discussed at the beginning. An equilibrated balance in the reaction rates of the different reactions in this complex system must be found, so that the initial reversible dehydrogenation reaction occurs at a significant high rate and that the hydrogenation reactions to the end-products is fast enough. A too high pressure (80 bar) will result in a decrease of the conversion, certainly due to unfavorable conditions for the first step of dehydrogenation of xylitol to xylose. A too low pressure (40 bar) will facilitate the base-catalyzed degradation of the aldehyde intermediates at the expense of their hydrogenation to the desired products.

Variations in the H₂ pressure on selectivity were also analyzed. In the continuous experiments, selectivity to EG and PG increased by increasing the pressure from 40 bar to 60 bar; further increase to 80 bar had little effect on these selectivities, however, since conversion was declined, the yield in the desired glycols EG was lower. These results are close to those obtained by Sun et al. [37] Other products concentrations were also dependent on the H₂ pressure. Selectivity to GLY and threitol also increased as the H₂ pressure increased, consistent with the results reported previously and the fact that hydrogenation reactions are favored compared to base-catalyzed reactions. On the other hand, selectivity to BDO's and FA decreased at the highest pressures. This catalyst was used under the optimized conditions in experiments conducted on the Chemtex pilot plant. The activity of the catalyst was not modified when a hydrogenated xylose aqueous solution derived from hemicelluloses was used instead

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of a xylitol aqueous solution. Stability of the catalyst is under investigation.

4. Conclusions

The hydrogenolysis of a biomass-derived C5 sugar alcohol, xylitol, was carried out in a trickle-bed reactor over a Ru/C catalyst to explore the influence on conversion and product distribution of operating conditions of sodium hydroxide concentration, hydrogen pressure at two temperatures 190 and 200 °C. This reaction offers the possibility for producing C2-C3 glycols. The proportion of each of these can be modified by the choice of the process conditions. The effects observed were explained as viewed from the reaction mechanism proposed in the literature. Increasing the base concentration in the range considered (xylitol/NaOH molar ratio = 0.1-0.2) increased the xylitol conversion by accelerating the retro-aldol condensation reaction without significantly degrading the intermediates. There was a preferable hydrogen pressure in the range 40-80 bar for xylitol conversion and high productivity of EG and 1,2-PDO which was found to be ca. 60 bar. On the other hand, the highest pressure decreased the amount of by-products butanediols and formic acid. Under the optimized conditions the catalyst was stable chemically and from the catalytic performances viewpoint. Biochemtex has started the development of a process that converts xylose-rich hydrolyzates from the hemicellulosic fraction of biomass materials.

References

- [1] G.W. Huber, S. Iborra, A. Corma, Chem. Rev. 106 (2006) 4044–4098.
- [2] A. Corma, S. Iborra, A. Velty, Chem. Rev. 107 (2007) 2411–2502.
- P. Mäki-Arvela, B. Holmbom, T. Salmi, D.Y. Murzin, Catal. Rev. Sci. Eng. 49 (2007) 197–340.
- [4] P. Gallezot, Chem. Soc. Rev. 41 (2012) 1538–1558.
- [5] M. Besson, P. Gallezot, C. Pinel, Chem. Rev., doi:10.1021/cr4002269.
 [6] C.-H. Zhou, J.N. Beltramini, Y.-X. Fan, G.Q. Lu, Chem. Soc. Rev. 37 (2008)
- [7] J. Wisniak, M. Hershkowitz, S. Stein, Ind. Eng. Chem. Prod. Res. Dev. 13 (1974)
- 232. [9] D. Callazat, N. Nicolaus, C. Elècho, D. Evortos, A. Dorrard, J. Catal. 180 (1909)
- [8] P. Gallezot, N. Nicolaus, G. Flèche, P. Fuertes, A. Perrard, J. Catal. 180 (1998) 51–55.

- [9] J.-P. Mikkola, T. Salmi, R. Sjöholm, P. Mäki-Arvela, Catal. Today 48 (1999) 73–81.
 [10] J.-P. Mikkola, H. Vainio, T. Salmi, R. Sjöholm, T. Ollonqvist, J. Väyrynen, Appl. Catal. A: Gen. 196 (2000) 143–155.
- [11] D.C. Elliot, T.A. Werpy, Y. Wang, J.G. Frye Jr, US 6 235 797 (2001).
- [12] A.M. Ruppert, K. Weinberg, R. Palkovits, Angew. Chem. Int. Ed. 51 (2012) 2564–2601.
- [13] R.R. Bottoms, US 2 335 731 (1943).
- [14] F. Conradin, G., Bertossa, J. Giesen, US 2 852 570 (1957).
- [15] I.T. Clark, Ind. Eng. Chem. 50 (1958) 1125-1126.
- [16] N.A. Vasyunina, A.A. Balandin, Y. Mamatov, Kinet. Katal. 4 (1963) 156–162.
- [17] N.A. Vasyunina, A.A. Balandin, Y. Mamatov, Kinet. Katal. 4 (1963) 443–449.
- [18] J.C. Chao, D.T.A. Huibers, US 4 366 332 (1982).
- [19] M. Dubeck, G. Knapp, US 4476 331 (1984).
- [20] B.J. Arena, US 4 401 823 (1983), US 4 496 780 (1985).
 [21] D.K. Sohounloue, C. Montassier, J. Barbier, React. Kinet. Catal. Lett. 22 (1983)
- 391–397.
- [22] C. Montassier, D. Giraud, J. Barbier, Stud. Surf. Sci. Catal. 59 (1988) 165–170.
- [23] C. Montassier, J.C. Ménézo, L.C. Hoang, C. Renaud, J. Barbier, J. Mol. Catal. 70 (1991) 99–110.
- [24] E. Tronconi, N. Ferlazzo, P. Forzatti, I. Pasquon, B. Casale, L. Marini, Chem. Eng. Sci. 47 (1992) 2451–2456.
- [25] K. Wang, M.C. Hawley, T.D. Furney, Ind. Eng. Chem. Res. 34 (1995) 3766–3770.
- [26] G. Gubitosa, B. Casale, US 5 354 914 (1994).
- [27] G. Gubitosa, B. Casale, US 5 600 028 (1997).
 [28] S. Chopade, D. Miller, J. Jackson, T. Werpy, J. Frye Jr, A. Zacher, US 6 291 725
- (2001). [29] T.A. Werpy, J.G. Frye Jr, A.H. Zacher, D.J. Miller, US 6 479 713 (2002).
- [30] D.G. Lahr, B.H. Shanks, J. Catal. 232 (2005) 386–394.
- [31] A.H. Zacher, J.G. Frye Jr., T.A. Werpy, D.J. Miller, in: J.R. Sowa Jr. (Ed.), Chemical Industries. Catalysis of Organic Reactions, vol. 104, CRC Press LLC, Boca Raton, FL, USA, 2005, pp. 165–173.
- [32] W.B. Hoffer, R. Prochazka, WO 2008071616, WO 2008071641, 2008071642 (2008).
- [33] L. Zhao, J.H. Zhou, Z.J. Sui, X.G. Zhou, Chem. Eng. Sci. 65 (2010) 30–35.
- [34] J.H. Zhou, M.G. Zhang, L. Zhao, P. Li, X.G. Zhou, W.K. Yuan, Catal. Today 147S (2009) S225–S229.
- [35] M. Banu, S. Sivasanker, T.M. Sankaranarayanan, P. Venuvanalingam, Catal. Commun. 12 (2011) 673–677.
- [36] N. Li, G.W. Huber, J. Catal. 270 (2010) 48-59.
- [37] J. Sun, H. Liu, Green Chem. 13 (2011) 135–142
- [38] L. Ye, X. Duan, H. Lin, Y. Yuan, Catal. Today 183 (2012) 65-71.
- [39] K.L. Deutsch, D.G. Lahr, B.H. Shanks, Green Chem. 14 (2012) 1635–1642.
- [40] H.-J. Arpe, Industrial Organic Chemistry, fifth completely revised version, Wiley-VCH, Weinheim, 2010.
- [41] N. Ji, T. Zhang, M. Zheng, A. Wang, H. Wang, X. Wang, J.G. Chen, Angew. Chem. Int. Ed. 47 (2008) 8510–8513.
- [42] A. Wang, T. Zhang, Acc. Chem. Res. 46 (2013) 1377–1386, and references cited herein.
- [43] Y. Liu, C. Luo, H. Liu, Angew. Chem. Int. Ed. 51 (2013) 3249-3253.