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Hydrogenation of sugars to sugar alcohols in the presence of a recyclable Ru/Al₂O₃ catalyst commercially available

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ABSTRACT

Nowadays, the catalytic conversion of lignocellulosic biomass is the topic of many investigations. Interesting compounds that can be produced from the carbohydrate part of lignocellulose are sugar alcohols. Hence, these products production is of prime interest due to their wide use in chemical

industries. They can be synthesized by the hydrogenation of sugar monomers in the presence of heterogeneous catalysts that are not always stable in water. Herein, we show that a commercial Ru/Al₂O₃ catalyst can be used to selectively convert first glucose to sorbitol with a yield around 97 % under optimized conditions. The reaction pathway was determined by the analysis of intermediate compounds. This catalyst was stable up to 10 reaction cycles due to the nature of the support and the Ru particle sizes. I was active in the hydrogenation of sugars such as glucose, fructose, mannose, galactose and xylose to sugar alcohols.

INTRODUCTION

Politics, socio-economic area and industrial sectors are faced with climate change and all the related consequences (reduction of biodiversity, global warming due to greenhouse gases emissions, ocean acidification, etc.) A major shift toward bio-products made from renewable feedstocks is an interesting alternative to decrease the environmental impact. A lot of research is devoted to the use of lignocellulosic biomass that can give access to a wide range of chemicals. Among them, sugar alcohols such as xylitol, sorbitol, mannitol are of prime interest. They can be used as sweeteners and due to their moisturizer and texturizer properties, they can be applied in pharmaceuticals, cosmetics sectors for toothpaste production for instance.¹⁻⁵ For example, sorbitol was considered in 2004 by the U.S. Department of Energy as a high-value bio-based chemicals to produce alkanes by hydrogenolysis for biofuels production as well as building blocks to produce chemicals such as glycols and isosorbide.⁶⁻⁸

Sugar alcohols can be produced from the catalytic hydrogenation of sugar monomers (contained in the carbohydrate part of lignocellulose). Nickel-based catalysts like Raney nickel promoted or not with transition metals (Cr, Fe, Sn, Mo) were firstly study and used at industrial level for the

hydrogenation of sugars to sugar alcohols.⁹⁻¹⁸ Thus, sorbitol is industrially produced from a glucose solution in both autoclave and trickle bed reactors at around 110-150°C. But the continuous process needs higher hydrogen pressure (100 bar against 40 to 70 bar in a batch process).^{1,13} However, in the presence of the Ni-based catalysts, the selectivity was low due to side reactions (degradation of sugars) because of high hydrogen pressure and temperature required in the hydrogenation of sugars to sugar alcohols. Moreover, Ni catalysts suffer from a lack of stability. To avoid metal leaching, noble metals with active sites for hydrogenation of sugar to sugar alcohols have been largely investigated and more specifically Ru and Pt.¹⁹⁻²¹ These metals were investigated supported on different support and it was shown that ruthenium was the most efficient in the selective hydrogenation of carbonyl to the corresponding alcohols.²²⁻²⁹ Among the studied support carbon-based materials,²⁷⁻³² oxides supports (Al_2O_3 ^{13,33}, TiO_2 ¹³, ZrO_2 , $\text{ZrO}_2\text{-Al}_2\text{O}_3$, phosphated zirconia, phosphated zirconia-alumina³⁴) and silica materials (SiO_2 ^{13,35}, SBA-15³⁵, ZrO_2 coated on SBA-15³⁶) as well as structured supports like zeolite (zeolite Y³⁷, BEA³⁸, H-ZSM-5³⁹) mesoporous silica MCM-48⁴⁰ and Linde type L zeolite-MCM41⁴¹ were investigated. In all these studies, it appears that the control of the selectivity and the catalyst deactivation are the main points that should be addressed in the synthesis of sugar alcohols. Moreover, based on the high cost of Ru the most active one, it is necessary to design an active and selective catalyst with the lowest possible cost that can be recyclable. Although, the particle size of Ru is important in the hydrogenation of sugars to sugar alcohols, a particular attention should be devoted to this parameter.³² Al_2O_3 appears as an interesting support based on its high surface and strong mechanical solidity but it suffers from a lack of stability. Hence, Blaise J. Arena studied the deactivation of Ru/ Al_2O_3 catalyst in a continuous pilot at 120°C, under 150-160 bar of hydrogen for the hydrogenation of an aqueous solution of glucose.³³ They demonstrated that several

compounds were responsible of the poisoning of Ru species such as gluconic acid, sulfur and iron. In another study¹³ the hydrogenation of an aqueous solution of glucose in an autoclave at 120°C and at a high hydrogen pressure of 120 bar in the presence of a Ru/Al₂O₃ catalyst led to a selectivity of sorbitol lower than 70 % (60-65 %) in a batch process due also to poisoning of the active sites. In order to prevent the deactivation of a Ru/Al₂O₃ catalyst, a newly synthesized core-shell-like sphere ruthenium catalyst, named 5%Ru/γ-Al₂O₃@ASMA, ruthenium nanoparticles (NPs) supported on an amino poly (styrene-co-maleic) polymer (ASMA) encapsulating γ-Al₂O₃ pellet support was found to be stable and 95% yield of sorbitol was obtained under 50 bar of hydrogen at 120°C for 2h of reaction.⁴² The stability of the catalyst was due to the encapsulation of γ-Al₂O₃ by a polymer. Based on these studies, Ru/Al₂O₃ catalyst suffers from a lack of stability and leads to a selectivity lower than 70%. Thus, the search for a stable catalyst commercially available that can be used in the hydrogenation of sugars to sugar alcohols by preventing secondary reactions is still demanded.

Herein, we report the use of a recyclable commercially available Ru/Al₂O₃ catalyst in the hydrogenation of various sugar monomers to sugar alcohols with high selectivity. We demonstrate that Ru/Al₂O₃ catalyst with appropriate particle sizes and a support composed of different alumina phases was efficient in the hydrogenation of an aqueous solution of sugars to sugar alcohols. In the hydrogenation of glucose to sorbitol, under optimized conditions, a 97% sorbitol yield was obtained in a batch process in the presence of water as a solvent. Ru/Al₂O₃ recyclability was also demonstrated based on the control of secondary reactions that limit the poisoning of the catalyst due to the nature of the support. Ru/Al₂O₃ catalyst was also active and selective in the hydrogenation of various sugars such as fructose, mannose, galactose and xylose.

EXPERIMENTAL

Catalytic tests and analysis

A Multiple Reactor System Series 5000 by Paar Instrument Company was used for hydrogenation reactions. In a typical hydrogenation reaction, a prepared mixture of 2 g of sugar dissolved in 18 g of ultra-pure water (10 wt. % of sugar in water) was placed in a glass vessel and 0.1 g of reduced catalyst (under H₂ at 200°C for 2 h) was subsequently added to the mixture. The glass vessel was inserted in the reactor and this last was sealed and flushed by N₂ three times. The experiment was started when 30 bar of H₂ was introduced into the reactor (t = 0 min) at 120°C for the desired reaction time. Agitation and heater were stopped at the end of the experiment and hydrogen was removed when the reactor was cool down to ambient temperature. The catalyst was removed from the reaction media and the liquid phase was filtrated by a syringe filter and diluted in ultra-pure water before analysis that was performed with a High Performance Liquid Chromatography (HPLC). To this end a Shimadzu HPLC with a Refractive Index Detector (RID) was used to quantify sugars products. An anion-exchange column (CarboSep CHO 820-Ca²⁺ 300 mm x ID 7.8 mm) was employed with ultra-pure water as an eluent with 0.5 mL min⁻¹ flow rate. The column temperature was fixed to 80°C.

Catalyst characterization

The catalysts were characterized by using surface area analysis and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) for the Ru content. The structure of the catalysts was characterized by XRD, TEM, SEM, and TGA before and after catalytic test. The results and details of each technique has been provided in supplementary document.

RESULTS AND DISCUSSION

In a first set of experiments, a screening of commercial catalysts with 4 to 5 wt% metal loading (Table S1) Pt/Al₂O₃, Pd/Al₂O₃ and Ru/ Al₂O₃ were investigated in the hydrogenation of 10 wt.% of glucose in water to sorbitol (Figure 1) at 120°C under 30 bar of H₂. The reaction was performed first in the absence of catalyst and 16% of glucose was converted but the yield of sorbitol was only 2%. The reaction media was light brown at the end of the reaction probably due to the degradation of glucose to humins.

Table 1. Screening of commercial noble metal catalysts for the hydrogenation of glucose into sorbitol under 30 bar H₂ at 120°C for 1 h with 10 wt.% of glucose (2 g) in 18 g of water and 5 wt.% of catalyst

Catalyst	Glucose conversion (%)	Sorbitol yield (%)	Sorbitol selectivity (%)
none	16	2	11
Pd/Al ₂ O ₃	3	1	33
Pt/Al ₂ O ₃	8	1	12
Ru/Al ₂ O ₃	100	80	80

Surprisingly, Pd/Al₂O₃ and Pt/Al₂O₃ catalysts are less active than the blank test, the conversion of glucose being negligible probably due to the limitation of side reactions. Hence, the reaction media was colorless in the presence of Pd/Al₂O₃ and Pt/Al₂O₃ catalysts whereas it was light brown in the absence of a catalyst. The highest selectivity to sorbitol (80%) at a full conversion of glucose was obtained in the presence of Ru/ Al₂O₃.

To further investigate the catalytic properties of Ru/Al₂O₃, the conversion of glucose and the yield of sorbitol were plotted versus time for the reaction in the presence of Ru/Al₂O₃ catalyst (Figure 1). After 90 min of reaction, a full conversion of glucose was obtained in the presence of Ru/Al₂O₃ catalyst with a sorbitol yield of 87%. Upon prolonged reaction time (5h) no degradation of the produced sorbitol was observed showing the stability of the product under these reaction conditions. Indeed, even if a slight decrease of sorbitol yield is observed after 180 min of reaction, it is in the margin error of the analysis. One can mention that fructose was observed at the beginning of the reaction followed by the formation of mannitol after 1 hour of reaction (Fig. S1). Fructose comes from glucose isomerization and we can assume that mannitol is produced by the hydrogenation of fructose. In order to confirm this hypothesis, a reaction was conducted starting from fructose in the presence of Ru/Al₂O₃ catalyst under similar conditions and the conversion of fructose reached 100% after 2 h of reaction with 40% yield of mannitol and 53% yield of sorbitol. Moreover, a reaction was performed starting from mannitol and only traces of sorbitol, below 1%, was produced confirming that the isomerization of mannitol was not responsible of the major formation of sorbitol under these conditions in the presence of Ru/Al₂O₃ catalyst. Moreover, traces of iditol was observed after 1h30 of reaction due to the the high concentration of sorbitol at the end of the hydrogenation reaction that leads to the isomerization of sorbitol to iditol.⁴³

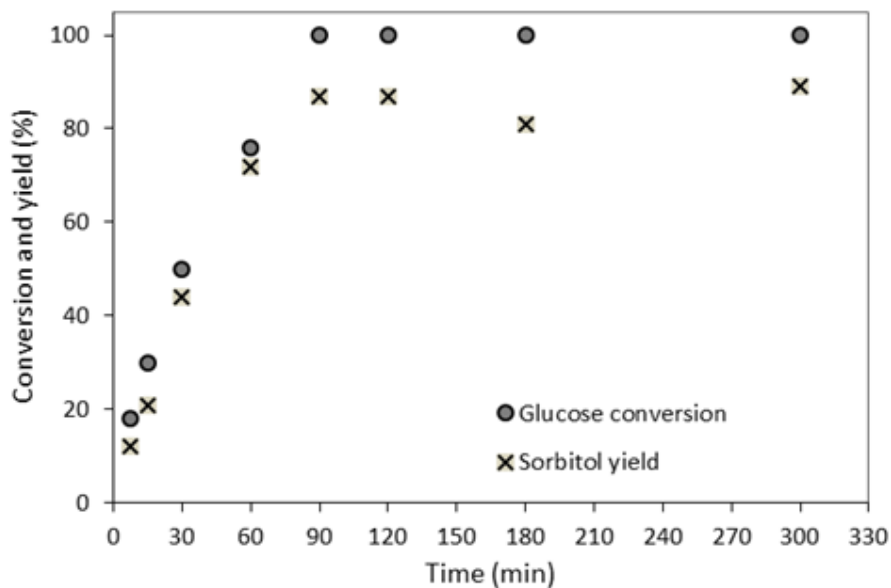
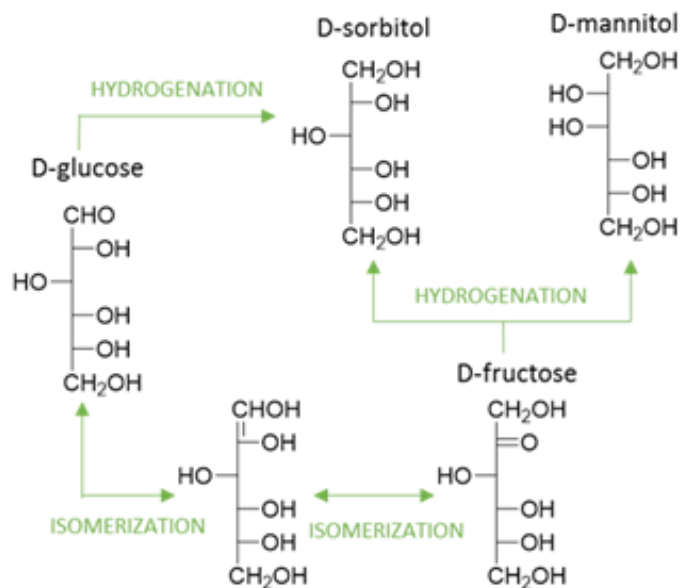


Figure 1. Hydrogenation of glucose into sorbitol according to time reaction in the presence of 5 wt.% of Ru/Al₂O₃ catalyst under 30 bar H₂ at 120°C starting from 10 wt.% of glucose in water.

The reaction pathway for the hydrogenation of glucose to sorbitol in the presence of Ru/Al₂O₃ catalyst is thus described in scheme 1. Based on the analysis of the reaction intermediates, sorbitol can be produced through two pathways in the presence of this catalyst. One route is the isomerization of glucose to fructose that can be hydrogenated to sorbitol and mannitol. The other route is the direct hydrogenation of glucose to sorbitol. Based on the results obtained, the main pathway to obtain sorbitol under these conditions is the direct hydrogenation of glucose since only slight amount of mannitol is observed during the reaction. This catalyst is very selective to sorbitol and secondary reactions are limited.



Scheme 1. Glucose hydrogenation to sorbitol pathway in the presence of Ru/Al₂O₃ catalyst.

Catalysts stability is one of the most recurrent bottleneck reported in literature because of lixiviation, sintering or poisoning effects. Thus, the recycling of Ru/Al₂O₃ was studied (Figure 2). The reaction was performed using similar conditions of pressure and temperature during 1h30. After the reaction, the catalyst was recovered by centrifugation of the reaction media and it was washed several time with ethanol. Then, the solid was dried at 50°C prior to a new cycle without any treatment. We were pleased to see that there were no significant loss in conversion of glucose and sorbitol yield up to 10 cycles. After the 6th cycle, only 13 ppm of Ru was found in the reaction media by ICP AOS analysis. In order to confirm that it was a heterogeneous catalysis, the hydrogenation of glucose was performed for 30 min and the catalyst was removed. The liquid mixture was heated up to 120°C under 30 bar of H₂ for 1 h and no increase in the sorbitol yield was observed. This result demonstrates that the Ru in solution is not active in the hydrogenation of glucose to sorbitol.

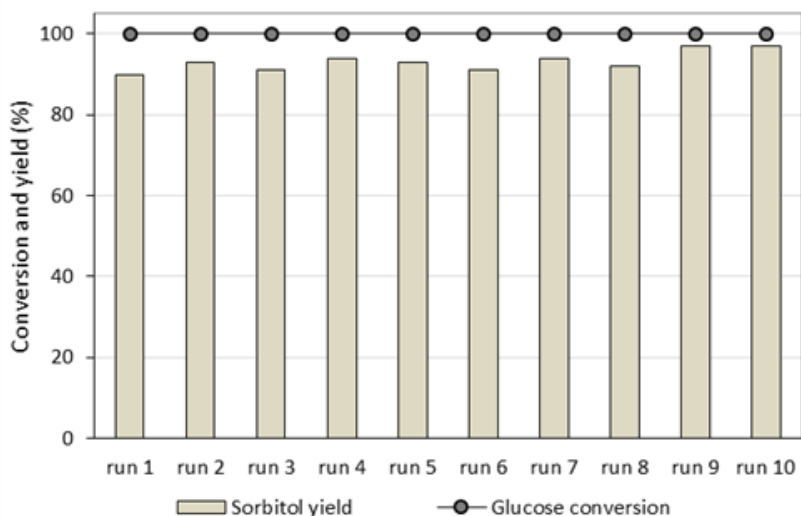
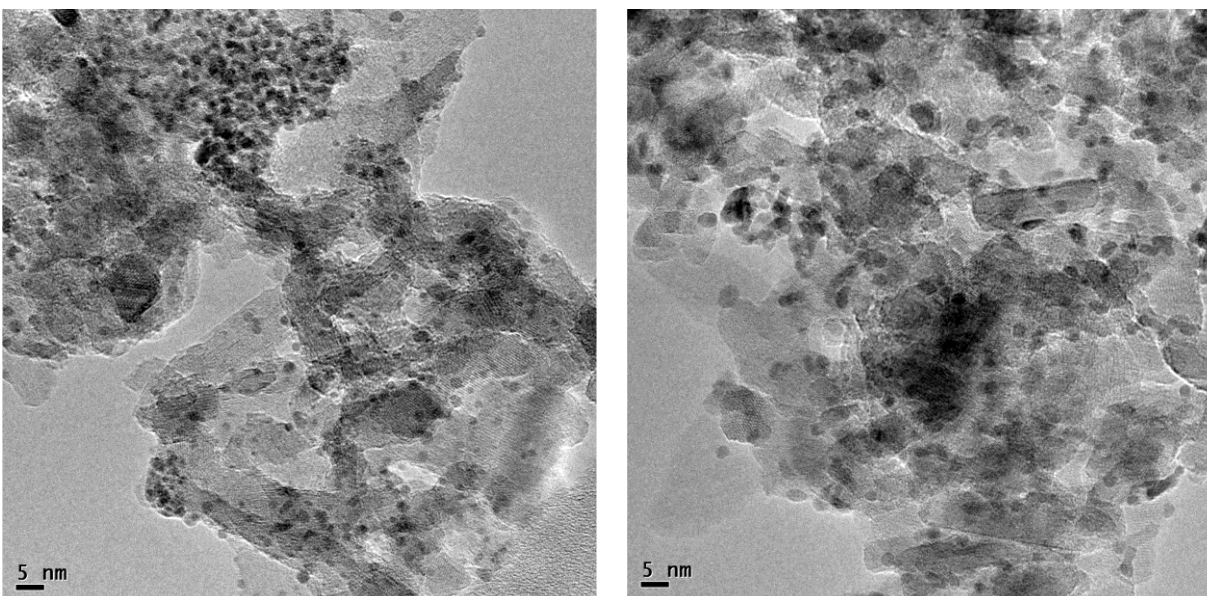


Figure 2. Recycling Ru/Al₂O₃ in the hydrogenation of glucose into sorbitol in the presence of 5 wt.% of Ru/Al₂O₃ under 30 bar H₂ at 120°C starting from 10 wt.% of glucose in water.

The catalyst was characterized after reaction and was compared to the fresh catalyst. The specific surface remains similar after the reaction (around 140 m²/g), there is only a decrease of the pore size from 178 to 166 Å (Fig. S2 and Table S2). Hence, thermal analysis were performed and it was clear that some compounds were adsorbed on the catalytic surface after recycling (around 8%) (Fig S3). Despite the adsorption of some compounds, the catalyst was recyclable. In order to pay attention to the nature of the support, XRD analyses were performed and show no change in the crystalline structure of the support (Fig. S4) that was composed of two aluminium oxide phases. It was a gamma alumina with a tetragonal structure phase associated with a monoclinic one. The presence of the two phases can enhance the stability of the catalyst by helping to disperse the active species. From TEM analysis, it was shown that Ru particles size was almost unchanged being around 2.5 nm (Fig. S5). One interesting observation was that the Ru dispersion seems to increase during the recycling which surely helps to prevent the deactivation of the catalyst (Figure 3).



Ru/Al₂O₃ catalyst

Spent Ru/Al₂O₃ catalyst (after the third run)

Figure 3. TEM analysis of fresh and spent Ru/Al₂O₃ catalyst.

Based on all these characterizations, it appears that Ru/Al₂O₃ catalyst is relatively stable under these conditions in the hydrogenation of glucose to sorbitol in water due to the particle sizes of Ru that is around 2.5 nm³² and the nature of the support³⁴ has an effect as reported in the literature. This alumina support is appropriate in order to prevent strong poisoning of the catalyst by controlling the selectivity of the reaction.

The experimental conditions were then studied. First, the effect of the hydrogen pressure was investigated (Figure 4). A decrease in glucose conversion was observed at 10 bar and 20 bar surely because of a lower solubility of H₂ in the reaction mixture. Higher pressure are needed (higher than 20 bar) to convert 100 % of glucose and to reach a sorbitol selectivity of 80 % when 30 bar of H₂ is used and 90 % when 40 bar of H₂ is used. However, the selectivity of the reaction was almost unchanged with the variation of the hydrogen pressure. Interestingly, fructose was observed for a pressure below 20 bar (around 2%) along with some traces of mannitol. For a H₂ pressure

higher than 20 bar no fructose was detected and 5% of mannitol was produced. It is supposed that a high concentration of dissolved H₂ can further hydrogenated fructose into mannitol.

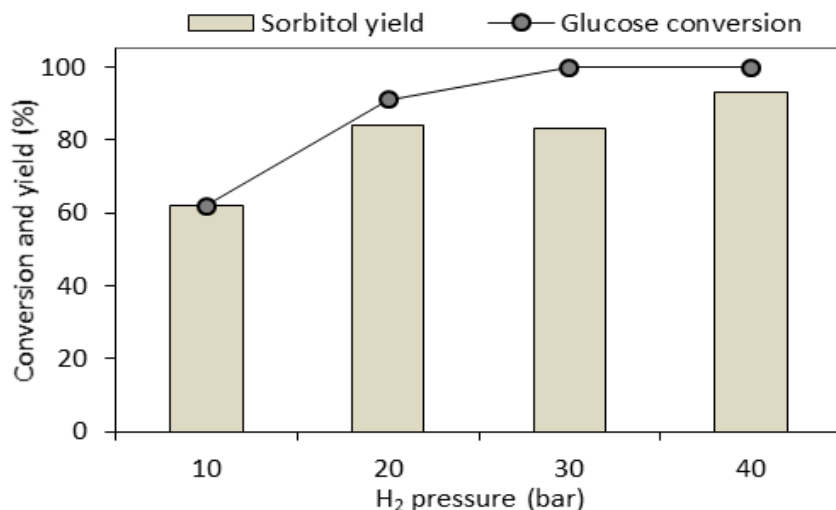


Figure 4. Effect of the hydrogen pressure in the hydrogenation of glucose into sorbitol in the presence of 5 wt.% of Ru/Al₂O₃ at 120°C with 10 wt.% of glucose in water for 2h00.

Secondly, the influence of reaction temperature was investigated (Table 2). When the temperature was decreased from 120°C to 100°C, 100% of glucose conversion can be reached but after 2h30 instead of 1h30 at 120°C. It was interesting to see that the selectivity was higher (97%) at 100°C than at 120°C (84%) but upon prolonged reaction time. At 90°C similar trend was observed than at 100°C after 2h of reaction. At 80°C the activity of the catalyst was too low since the conversion of glucose was only 38% after 2h of reaction. An experiment at 140°C was carried out for 1h, a total conversion of glucose was observed with a selectivity to sorbitol of 77%. From these results we can point out that 97% yield of sorbitol can be reached at a mild temperature of 100°C but after 2.5 h of reaction.

Table 2. Effect of reaction temperature for the hydrogenation of glucose into sorbitol in the presence of 5 wt.% of Ru/Al₂O₃ under 30 bar H₂ with 10 wt.% of glucose in water.

Temperature (°C)	Time (h)	Glucose conversion (%)	Sorbitol yield (%)	Sorbitol selectivity (%)
80	2	38	32	83
90	2	65	63	97
100	2	61	60	98
100	2.5	100	97	97
120	2	100	84	84
140	1	100	77	77

The weight percentage of catalyst Ru/Al₂O₃ was then studied (Figure 5). A decrease of the catalyst loading from 5 wt.% to 2.5 wt.% led to similar yield of sorbitol around 85% with a full conversion of glucose. Interestingly, a further decrease of the catalyst amount to 1 wt.% led to a slight decrease of the conversion down to 91% with 90% yield of sorbitol. The reaction was thus very selective in the presence of a low amount of catalyst. These results showed that the catalyst loading can be decreased up to 1 wt.%. On the opposite an increase of the catalyst loading from 5

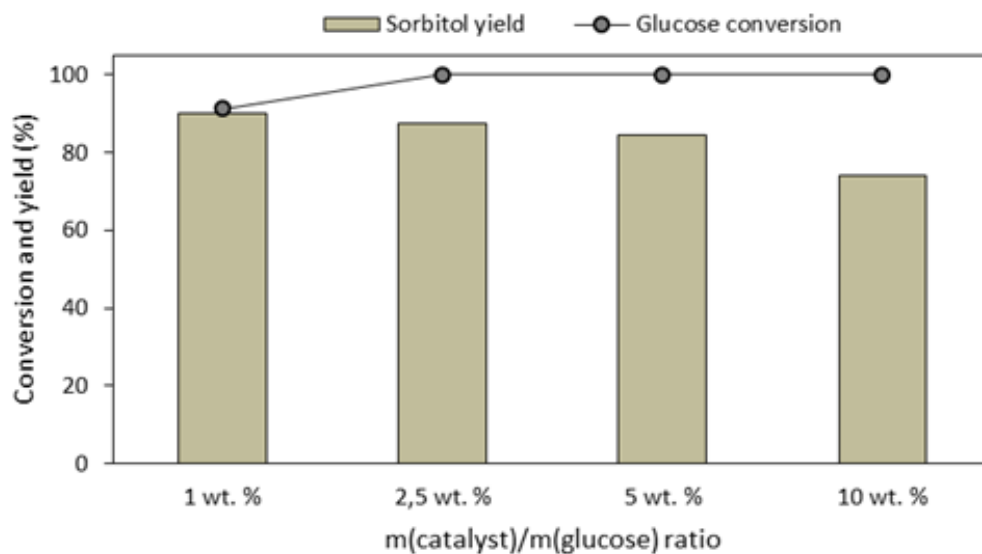


Figure 5. Hydrogenation of glucose into sorbitol according to wt% of Ru/Al₂O₃ under 30 bar H₂ at 120°C with 10 wt.% of glucose in water for 2h00.

to 10 wt.% led to a decrease in the selectivity to sorbitol due to the formation of unknown by-products as well as the isomers of sorbitol (mannitol, iditol). The reaction media was coloured indicating that in the presence of a high amount of catalyst some degradation reaction of glucose can occur. Thus, it is necessary to adjust catalyst amount in order to increase activity and reaction rate as well as selectivity to avoid side reactions.

This catalyst was then used in the hydrogenation of various sugars such as fructose, mannose, galactose and xylose (Table 3).

We were pleased to see that Ru/Al₂O₃ was also active in the hydrogenation of other carbohydrates such as fructose, mannose, xylose and galactose under the optimized conditions described before. All monomers were converted in their respective hydrogenated products with a selectivity from 92 to 53%. Galactose hydrogenation can provide at least 60 % crystallized galactitol and its purity

was confirmed by NMR 1H (Fig. S6). Only the hydrogenation of fructose led to a mixture of sugar alcohols that was sorbitol and mannitol mixture.

Table 3. Hydrogenation of sugars in the presence of 5 wt.% of Ru/Al₂O₃ under 30 bar H₂ at 120°C from 10 wt.% of glucose in water for 2h.^[a]

Sugars	Sorbitol yield (%)	Mannitol yield (%)	Galactitol yield (%)	Xylitol yield (%)
Fructose	53	40		
Mannose		84		
Galactose			60	
Xylose				92

[a] Full conversion in all experiments

CONCLUSION

The selective hydrogenation of sugars is still requiring recyclable catalysts that are stable in water with a low amount of noble metal. Here, we demonstrate that a Ru/Al₂O₃ catalyst with 5 wt% of Ru is active and selective in the hydrogenation of glucose and other sugars to sugar alcohols. This was due to the particle sizes of Ru that was around 2.5 nm and to the control of secondary reactions that limit the poisoning of the catalyst by appropriate alumina support. The catalytic amount can be decreased down to 1 wt.% with 90% yield of sorbitol in the hydrogenation of glucose. Moreover, the reaction can be performed at 100°C reaching a sorbitol selectivity of 97% for a total conversion of glucose in the presence of a catalyst that can be recyclable up to 10 cycles. Moreover, this catalyst can be applied in the hydrogenation of a wide range of sugars such as fructose, mannose, galactose and xylose.

ASSOCIATED CONTENT

ESI contains detailed description about catalyst characterization methodology and techniques such XRD, TEM, TGA, ICP-OES, Nitrogen adsorption-desorption analysis. It also includes NMR analysis of galactitol and materials used.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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SYNOPSIS

The present work is on the use of a recyclable Ru/C catalyst commercially available for the hydrogenation of sugars to sugar alcohols.

TOC

