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# A One Step Synthesis Of C6 Sugar Alcohols From Levoglucosan And Disaccharides Using A Ru/CMK-3 Catalyst

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#### Abstract

Sorbitol is an important commercially available chemical with a broad application range and is typically made by the catalytic hydrogenation of glucose. Here we report a high yield synthesis of sorbitol from levoglucosan (1.6-anhydro- $\beta$ -D-glucopyranose) and cellobiose, two sugars present in pyrolysis liquids, using a mesoporous carbon supported Ru catalyst (Ru/CMK-3). The hydrogenation reactions were performed in a batch autoclave set-up under a hydrogen pressure of 50 bar and temperatures ranging from 120 to 180  $^{\circ}$ C in water. The hydrogenation of levoglucosan gave essentially quantitative yields of sugar alcohols, composing of 96.2 wt.% of sorbitol and 3.8 wt.% of mannitol (180 °C, 5 h). Ru/CMK-3 shows superior catalytic performance compared to a commercial Ru/C catalyst. A reaction pathway involving glucose as an intermediate and subsequent (hydrogenolysis) reactions of the desired sorbitol is proposed. Reactions with glucose and sorbitol were performed to define the reaction pathways and to highlight the differences between Ru/C and Ru/CMK-3. Disaccharides including cellobiose and sucrose were also tested, yielding up to 95 wt.% of C6 sugar alcohols at 180 °C in 5 h for both substrates. Detailed catalyst characterization studies  $(N_2 \text{ physisorption}, \text{TEM}, \text{XRD}, \text{NH}_3\text{-}\text{TPD}, \text{H}_2\text{-}\text{TPD})$  revealed that Ru/CMK-3 contains considerable amounts of strong acid sites (NH<sub>3</sub>-TPD). Catalyst stability was tested by catalyst recycling experiments using levoglucosan in batch. After 3 successive runs, the rate of the hydrolysis reaction of LG to glucose was about constant, though the subsequent hydrogenation reaction to sorbitol/mannitol was slightly retarded as evidenced from a slight increase in the remaining amounts of glucose at the end of reaction.

Keywords: levoglucosan, pyrolysis liquids, sorbitol, Ru/CMK-3, hydrogenation

# 1.Introduction

Sorbitol is listed as one of the top 12 bio-based building blocks by the U.S. Department of Energy<sup>1</sup>. It is widely used as an additive in many industrial products, particularly in the food, cosmetic, and paper industry, but also as a building block for the synthesis of various fine chemicals including vitamin C<sup>2</sup>. The global production of sorbitol was 700,000 t/a in 2007<sup>3</sup> to over 1,000,000 t/a in 2009<sup>4</sup>. The overall capacity of sorbitol was 1,700,000 t/a in 2011 with an estimated growth rate of approximately 30 % per year<sup>5</sup>.

In the last decade, sorbitol has also been proposed as a starting material for biofuels and hydrogen production using aqueous phase reforming<sup>6</sup>. Another example is the conversion of sorbitol to isosorbide, an interesting biobased diol for the synthesis of polyesters (e.g. PET) and a range of other polymers<sup>1</sup>. The synthesis of isosorbide from sorbitol is typically carried out at temperatures between 160–180 °C using strong mineral or organic Brønsted acids such as sulfuric acid or *p*-toluenesulfonic acid in aqueous solutions.<sup>7</sup>

Nowadays, the production of sorbitol is solely accomplished by the catalytic hydrogenation of glucose<sup>8-15</sup>. The latter is obtained by hydrolysis of various starches like corn, rice, potato, and so forth. However, there is a strong incentive to use non-food glucose precursors for the production of sorbitol. An example is the use of cellulose, which can be converted to glucose (and subsequently to sorbitol) by a number of technologies.<sup>16-29</sup> Disadvantageously, yields are not on par and major breakthroughs are required before large scale commercial operation become economically viable.

Fast pyrolysis<sup>30</sup> is an alternative method for the depolymerization of lignocellulosic biomass and offers good prospective for the production of inexpensive low molecular weight sugars. It involves heating a solid biomass in the absence of oxygen, at atmospheric pressure and temperatures ranging from 300 to 600°C to yield a condensable liquid product referred to as pyrolysis liquids with yields up to 70 wt.%. Fast pyrolysis liquids contain considerable amounts of monomeric and oligomeric (anhydro)-sugars such as levoglucosan (the most abundant one), cellobiosan and glucose. The exact amounts are depending on the reactor configuration, feed, and process conditions, but are as high as 20.5 wt.% on biomass feed for red oak, see Table 1 for details. By using isolated cellulose as the feed, levoglucosan is the major product with yields up to 60 wt.%.<sup>31, 32</sup>

Table 1 Overview of reported amounts of low molecular weight sugars in pyrolysis liquids and sugar fractions derived thereof

Entry	Feed	Reactor Type	Analytical method	Sugar Content	Ref.
1	Red oak	Fluidized bed reactor	GC/MS, HPLC	20.62 ±2.52 wt.% (levoglucosan,	33
				cellobiosan, glucose, etc) in pyrolysis liquids	
				based on biomass feed	
2	Birch wood	CDS Pyroprobe 100 combined	GC/MS	15.3 wt.% of levoglucosan in pyrolysis	34
	sawdust	with a gas chromatograph (CP 9000)		liquids based on dry biomass feed	
3	Pine wood	Auger reactor	GC/MS	16.43±0.71 wt.% of levoglucosan in organic	35
				fraction of the pyrolysis liquids	
4	Red oak	Free fall reactor	HPLC	8 wt.% (levoglucosan, cellobiosan, xylose,	36
				etc) in pyrolysis liquids based on feed	
5	Mallee wood	Fluidized bed reactor	GC–MS	6 wt.% levoglucosan in pyrolysis liquids	37
6	Sugarcane	A CDS 5200 micropyrolyzer	GC-MS	23.45 wt.% of levoglucosan in pyrolysis	38
	bagasse	coupled to a GC-MS		liquids based on biomass feed	
7	Switch grass	A Frontier Lab Double Shot	GC-MS	15 wt.% of levoglucosan in pyrolysis liquids	39
		Micropyrolyzer 2020iS coupled		based on biomass feed	
		to a Varian 450 GC			
8	Red oak	Twin-screw auger reactor	HPLC	16 wt.% of xylose and glucose hydrolyzable	40
				sugars in the pyrolysis liquids	
9	Pine wood	Fluidized bed reactor	GC-MS	35 wt.% of levoglucosan in condenser 1	41
	and bagasse				
10	Pine wood	Transport bed reactor	Brix method	35 wt.% ether-insoluble sugar fraction in	42
				pine derived pyrolysis liquids	

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Pyrolytic sugars, isolated fractions of pyrolysis liquids enriched in sugars, can be obtained using staged condensation of the vapors formed during fast pyrolysis<sup>43</sup> (Table 1, Entry 1, 8, 9) or solvent fractionation of isolated pyrolysis liquids<sup>44</sup>. In the latter case, water is added to pyrolysis liquids and this results in a water soluble and water insoluble phase. The water soluble phase is comprised of sugars, organic acids, small aldehydes, ketones and water soluble lignin monomers, which can be separated using solvent extraction schemes (Table 1, Entry 10).

The application of pyrolytic sugars as the precursors for bio-ethanol by hydrolysis (for example using sulfuric acid) followed by fermentation has been studied before<sup>45-49</sup>. Besides, their conversion to platform chemicals such as 5-HMF, levulinic acid and levulinic esters in various solvents has also been investigated<sup>50, 51</sup>. Another example involves the use of the aqueous sugar fraction of pyrolysis liquids for the synthesis of hydrogen, alkanes and polyols by aqueous phase reforming<sup>52</sup>. The sugars were readily hydrogenated, however levoglucosan showed a very low rate of hydrogenation at 125  $^{\circ}$ C using Ru/C as the catalyst. At elevated temperatures (170 °C in 9 h), 28 mol.% of sorbitol (based on levoglucosan and sugars) was formed (68.9 bar H<sub>2</sub>). Sanna et al.<sup>53</sup> recently reported the hydrogenation of aqueous fractions of pyrolysis liquids with Ru/C at 125  $^{\circ}$ C under 50 bar (H<sub>2</sub> flow rate 150 ml/min) in a continuous set-up. The sorbitol yield was about 75 mol.% (based on levoglucosan and glucose), whereas substantial amounts of C1-C4 alcohols were formed as well. Li et al.54 reported the electrocatalytic hydrogenation of the aqueous phase of pyrolysis liquids using Ru supported on activated carbon cloth at 27 °C under atmospheric pressure and found that alcohols and glycols are the main products after 6.5 h reaction time. However, information regarding the sorbitol yield was not reported. Thus, sorbitol formation from the sugar fractions of pyrolysis liquids is feasible though the yield is still far from quantitative.

In this paper, we report (model component) studies aiming at the efficient conversion of levoglucosan and other low molecular weight sugars present in pyrolysis liquids to sugar alcohols and particularly sorbitol (Scheme 1), preferably in a single pot reaction.



Scheme 1 Proposed strategy for conversion of levoglucosan to sorbitol.

For an efficient conversion of levoglucosan to sorbitol, two reactions are of relevance, *viz.* i) the hydrolysis of levolglucosan to glucose, followed by the hydrogenation of glucose to sorbitol (Scheme 1). Hydrogenolysis and the formation of smaller diols such as glycerol and propylene glycol from glucose must be avoided, as well as subsequent acid catalyzed conversions of glucose to 5-HMF and levulinic acid. Proof of concept for the hydrolysis of levoglucosan is available in the literature using sulfuric acid as a Brønsted acid catalyst<sup>45,46</sup>. Both supported Ru (e.g. Ru/C) and Ni catalysts (e.g. Raney Ni) are known catalysts for glucose hydrogenation<sup>13,14</sup>. However, the use of inorganic acids for the hydrolysis reaction is not preferred as these are highly corrosive and neutralization is required to dispose of the acid after reaction. Thus, it is imperative to find catalysts for one step conversion of levoglucosan to sorbitol without the use of a homogeneous acid.

So far, only one study on the hydrogenation of levoglucosan has been reported. Bindwal *et*  $al.^{55}$  reported that ethylene glycol (4.7 wt.%), 1,2-propanediol (28.6 wt.%) and 1,4-butanediol (1.8 wt.%) are the main products for the hydrogenation of levoglucosan in water (140 °C, 20 bar H<sub>2</sub> pressure, 2 h batch time) using a conventional Ru/C catalyst. Sorbitol was not detected, indicating that hydrogenolysis occurs to a large extent. A reaction pathway was proposed involving initial hydrolysis of levoglucosan to glucose, hydrogenation to sorbitol and subsequent hydrogenolysis reactions of sorbitol to smaller diols. The reactions were carried out in the absence of a Brønsted acid, which may affect the product portfolio to a significant extent.

We anticipated that the use of supported bifunctional catalysts which possess acid sites for the hydrolysis reaction and an active (noble) metal for the hydrogenation reaction could be advantageous to achieve high C6 sugar alcohol yields from levoglucosan. Such supported bifunctional catalysts have also been applied for the conversion of cellulose to sugar alcohols. In this case, cellulose first undergoes hydrolysis to give oligomers and ultimately glucose over acidic sites, and the glucose is subsequently hydrogenated over metal catalysts to

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sorbitol and mannitol.<sup>23, 28, 56</sup> As such, there is a strong analogy with the proposed route for sorbitol from levoglucosan.

Here, we report studies on the hydrogenation of levoglucosan in water to C6 sugar alcohols and particularly sorbitol using a bifunctional Ru catalyst on a mesoporous carbon support (CMK-3). This support is characterized by a large surface area and a highly oxygenfunctionalized surface containing acid sites<sup>57</sup>. For instance, Ru/CMK-3 (in the absence of hydrogen) was reported to be a water-tolerant and reusable catalyst for the hydrolysis of cellulose<sup>58</sup> to low molecular weight sugars, indicating the presence of acid sites. For comparison, hydrogenation of levoglucosan using a commercial Ru/C catalyst was also carried out. The proposed reaction pathway was confirmed by performing catalytic hydrogenation experiments with glucose and sorbitol using both catalysts to identify the origin of the superior performance of Ru/CMK-3. In addition, the scope of the catalytic reaction was investigated by performing reactions with disaccharides like cellobiose and sucrose. Various techniques (nitrogen physisorption, X-ray diffraction (XRD), transmission electron microscopy (TEM), NH<sub>3</sub>-temperature programmed desorption (NH<sub>3</sub>-TPD) and H<sub>2</sub>temperature programmed desorption (H<sub>2</sub>-TPD)) were used to gain insights in the texture and acidity of the Ru/CMK-3 catalyst. Finally, catalyst stability was investigated by performing a number of batch experiments with recycled catalyst.

# 2. Experimental procedures

#### 2.1 Materials and methods

D-glucose ( $\geq$  99.5 %), D-sorbitol (99 %), D-mannitol ( $\geq$  98 %), glycerol ( $\geq$  99.5 %), 1,2propanediol ( $\geq$  99.5 %), 2-propanol (anhydrous, 99.5 %), sucrose ( $\geq$  99.5 %), RuCl<sub>3</sub> hydrate (Ruthenium content, 40.0 - 49.0 %) were purchased from Sigma-Aldrich and levoglucosan (1,6-anhydro- $\beta$ -D-glucopyranose), cellobiose (both from from Carbosynth, UK) were used as received. Polyvinylalcohol (PVA, 1 wt.% aqueous solution, Mw= 10000, 80 % hydrolyzed) was obtained from Aldrich. Ordered mesoporous carbon (CMK-3) with a BET surface area around 1000 m<sup>2</sup>/g, was supplied by ACS material, LLC. The elemental composition was determined by elemental analysis (C, 90.66 wt.%; H, 0.55 wt.%; O, 8.79 wt.%). Ru/C (5 wt.% Ruthenium loading) was obtained from KaiDa Technology Limited, UK, and was crushed and sieved to 25-75 µm before use. TEM images (Supplementary information, Figure S1) show the presence of Ru particles, that are not homogeneously distributed on the carbon surface. The particle sizes range from 20 to 50 nm. The particles are mainly in spherical form; however even Ru clusters with different shapes are present. Syringe filters (pore size 0.2  $\mu$ m, diameter 13 mm) were purchased from VWR international.

# 2.2 Preparation of Ru/CMK-3

Ru/CMK-3 (2 wt.% Ru on support), was prepared according to a published procedure<sup>59</sup>. RuCl<sub>3</sub> hydrate (45 mg) and a PVA solution (PVA to Ru weight ratio of 1 to 1.2) were dissolved in water (30 mL) and the mixture was diluted to 40 ml and stirred for 30 min at room temperature. 8 ml of a NaBH<sub>4</sub> solution in water (0.1 M, NaBH<sub>4</sub> to Ru molar ratio of 5) was added to the mixture and further stirred for 30 min, then acidified to pH 1 by the addition of a solution of sulfuric acid in water (1 M). Subsequently, the appropriate amount of CMK-3 to achieve a metal loading of 2 wt.% was added under vigorous stirring conditions. After 2 h, the slurry was filtered and the catalyst was washed thoroughly with distilled water and dried at 100 °C overnight.

# 2.3 Catalyst Characterization

**Gas physisorption:** Nitrogen physisorption analyses (-196.2  $^{\circ}$ C) were carried out in a Micromeritics ASAP 2020. The samples were degassed in vacuum at 350  $^{\circ}$ C for 10 h. The surface area was calculated using the standard BET and Langmuir methods.

**X-Ray diffraction (XRD)**: XRD analysis was performed using a Philips X-Pert diffractometer equipped with a Ni β-filtered Cu-Kα radiation ( $\lambda$ = 1.5406 Å) at 40 kV and 30 mA. Low angle data were collected over 2 $\theta$  angles from 0.8-5, with a step size of 0.005° at a scan speed of 0.0025°·s<sup>-1</sup>. Then, data were also collected over a 2 $\theta$  angles from 5 – 80°, with a step size of 0.04° at a speed of 0.013°·s<sup>-1</sup>. Identification of the diffraction peaks was performed on the basis of the JCPDS database of reference compounds.

**Transmission Electron Microscopy (TEM):** A Philips CM12 instrument equipped with a highresolution camera was used to acquire and elaborate TEM images. Powdered samples were dispersed in 2-propanol under ultrasound irradiation and the resulting suspension put dropwise on a holey carbon-coated support grid. Page 9 of 34

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NH<sub>3</sub> Temperature Programmed Desorption (NH<sub>3</sub>-TPD): Surface concentration of acidic sites was determined by using a conventional flow apparatus operating both in continuous and pulse mode. Before TPD experiments, the catalyst samples (~50 mg) were reduced, at atmospheric pressure, by flowing hydrogen (60 STP ml/min) in a linear quartz micro-reactor (I, 200 mm; i.d., 4 mm) from room temperature to 350 °C at a heating rate of 10 °C/min. Then, the samples were saturated for 30 min in flow of a gas mixture containing 5 vol.% of NH<sub>3</sub>/He at 150°C (flow rate of 25 ml/min). After purging in helium flow until a constant baseline level was attained, TPD measurements were performed in the temperature range 100–800 °C at a rate of 10 °C/min using helium (25 STP ml/min) as carrier flow. The evolved ammonia was detected by an on-line thermal-conductivity detector, calibrated by the peak area of known pulses of NH<sub>3</sub>.

H<sub>2</sub> Temperature Programmed Desorption (H<sub>2</sub>-TPD): Hydrogen temperature programmed desorption (H<sub>2</sub>-TPD) measurements were performed by using a U-shaped quartz microreactor (i.d., 4 mm) and reducing the catalyst (50-100 mg) in hydrogen flow (60 STP ml/min) at 350 °C. After the reduction treatment, the sample was cooled in flowing H<sub>2</sub> to room temperature; afterwards H<sub>2</sub> was shut off and the sample was purged with argon flow (50 STP ml/min) for 10 min. After purging, the desorption process was started by heating the sample up to 700 °C in the argon carrier, with a heating rate of 10 °C/min. The desorption process was monitored and quantified by a thermal conductivity detector (TCD) connected to a TCD. Calibration test was performed by injecting in the carrier gas a known amount of H<sub>2</sub> in order to obtain reliable quantitative measurements. Metal dispersion (D) was calculated by assuming a chemisorption stoichiometry H/Ru<sub>surface</sub>=1. Metal surface area (MSA) was calculated assuming a site density of 8.2 Å<sup>2</sup>/at for Ru, while the Ru crystallite diameter (d) was assuming a spherical shape of the metal particle: d (nm)=n/D (%), where "n" is 101 for Ru<sup>60</sup>.

# 2.4 Reaction procedures

**Catalysts reduction:** The Ru/CMK-3 catalyst was used as prepared. In case of Ru/C, a prereduction step was applied in the batch reactor. This involved charging the reactor (Parr autoclave, 100 ml, max. 350  $^{\circ}$ C and 350 bar) with 0.2 g of catalyst. The reactor was pressurized with 100 bar of N<sub>2</sub> to check for leakage, and then the reactor was depressurized. The reactor was flushed three times with 20 bar of H<sub>2</sub> to remove air and the Ru/C was prereduced at 350  $^{\circ}$ C under 2-30 bar H<sub>2</sub> for 1 h at a stirring speed of 800 rpm, before cooling to room temperature.

**Hydrogenation reactions:** A solution of levoglucosan (20 mmol in 40 mL, 0.5 M) or the disaccharides (10 mmol in 40 mL, 0.25 M) was injected into the reactor containing the catalyst from a feed vessel using pressurized N<sub>2</sub>. Then the reactor was flushed 3 times with H<sub>2</sub> (20 bar). The reactor was pressurized to 50 bar with additional H<sub>2</sub> and then heated to the desired temperature with a heating rate of around 10 °C/min at a stirring speed of 1400 rpm. Both reactor pressure and temperature was reached, the time was set as t = 0 h, the typical reaction time was 0.5-5 h. After reaction, a sample of the liquid phase was filtered using 0.2 µm filters, and then analyzed using HPLC. Hydrogenation experiments with sorbitol and glucose were carried out in a similar manner.

**Hydrolysis reactions:** The experimental procedure for the hydrolysis reactions of levoglucosan is the same as for the hydrogenation reactions, the only exception is the use of 50 bar of  $N_2$  instead of  $H_2$ .

**Recycling tests**: A typical levoglucosan hydrogenation experiment was performed with a 3 h batchtime. Subsequently, the spent catalyst was separated from the liquid phase by centrifugation (4500 rpm, 20 min). The spent catalyst was washed 3 times with 40 ml mili-Q water and then dried in an oven at 70 °C overnight. A second experiment was performed using the spent catalyst using the same procedure and conditions as for the first run.

# 2.5 Analytical methods

**HPLC analyses of the liquid phase:** The liquid phase after reaction was analyzed using HPLC. A HPLC apparatus equipped with a Hewlett Packard 1050 pump, a Bio-Rad organic acid column (Aminex HPX-87H) and a differential refractometer was used. The mobile phase consisted of an aqueous solution of sulfuric acid (5 mmol/l) operated at a flow rate of 0.55 cm<sup>3</sup>/min. The column was operated at 60 °C. The amount of the products was calculated using calibration curves obtained from standard solutions of known concentrations.

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# 3 Results and discussions

# 3.1 Characterization of Ru/CMK-3 and Ru/C

A detailed catalyst characterization study was performed to gain insights in the structural features (texture and acid sites) of Ru/CMK-3 as well as the Ru/C benchmark catalyst. The well-ordered mesoporous structure of CMK-3 and Ru/CMK-3 was confirmed by  $N_2$  physisorption. Both the CMK-3 support and the Ru/CMK-3 catalyst display a type IV isotherm with a characteristic H2 hysteresis loop in the relative pressure range from 0.4 to 0.9 (Figure S2, supporting information). The pore size distributions are provided in Figure S3 (Supporting information).

Sample	S <sub>BET</sub> (m <sup>2</sup> /g)	Vp (cm <sup>3</sup> /g) <sup>a</sup>	Dp (nm) <sup>b</sup>	APD <sup>c</sup> (nm)
CMK-3	990	1.20	4.7	4.8
Ru/CMK-3	913	1.09	4.6	4.7
Ru/CMK-3 (spent)	900	1.10	4.8	4.9
Ru/C	745 <sup>d</sup>	0.27	3.1	1.5

Table 2 Physicochemica	l properties of	<sup>E</sup> CMK-3 and Ru/CMK-3
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<sup>a</sup> Single point desorption total pore volume of pores less than 840.779 Å width at p/p° = 0.97 <sup>b</sup> BJH Desorption average pore width (4V/A). <sup>c</sup> Average Pore Diameter evaluated as 4PV/SA <sup>d</sup> SA Langmuir

The BET surface area of the CMK-3 used in this study was about 990 m<sup>2</sup>/g, as shown in Table 2, which is slightly lower than the value reported in the literature  $(1120 \text{ m}^2/\text{g})^{58}$ . Differences in synthetic procedures for CMK-3 are the plausible cause for this observation. The average pore diameter, as measured using the BJH method, was 5.0 nm, which is slightly higher than reported in the literature <sup>58</sup>. Upon introduction of Ru, the surface area decreases from 990 to 913 m<sup>2</sup>/g and the pore diameter reduces from 4.7 to 4.6 nm, most likely due to the incorporation of the small Ru nanoparticles in the pores or pore openings (*vide infra*).



Figure 1 Small and wide angle XRD patterns of CMK-3 and Ru/CMK-3

The well-ordered mesoporous structure of CMK-3 and Ru/CMK-3 was also confirmed by small angle X-ray diffraction (SAXRD), see Figure 1. The CMK-3 sample shows a very intense diffraction peak (100) and two low intense peaks (110) and (200), which are characteristic of a two-dimensional hexagonal structure <sup>61</sup>. The intensities of the XRD peaks for the Ru/CMK-3 sample are slightly reduced compared to the CMK-3 precursor, though the pattern is similar, indicating that the ordered structure is retained after introduction of Ru and the subsequent reduction step.

The wide-angle XRD spectra of CMK-3 and Ru/CMK-3 (Figure 1) show two intense diffraction peaks located at around 23 and 43°, corresponding to (002) and (101) diffractions of typical turbostratic carbon, respectively<sup>62</sup>. Clear diffraction peaks from Ru nanoparticles could not be detected, owing to the small dimensions of the Ru-particles (*vide infra*).

TEM images of CMK-3 and Ru/CMK-3 were recorded to gain insights in the position and the size of the Ru-nanoparticles (Figure 2). For both CMK-3 and Ru/CMK-3, uniform channels can be observed, confirming the structured mesoporous character of the support. Ru nanoparticles are present as clusters of different sizes (Figure 2b), and seem to be located preferentially on the CMK-3 edges. These TEM results are not in full agreement with the characterization study on Ru/CMK-3 performed by Komanoya *et al.* <sup>62</sup> where the presence of small Ru particles was observed with an average particle diameter of 1.1 nm. In our case, the particles are slightly larger (and agglomerated) and between 1.7-2.3 nm (Figure 2d). These differences are likely due to the catalyst preparation procedures, *viz.* a colloidal precipitation

and chemical reduction procedure with  $NaBH_4$  at low temperature in this study versus a wet impregnation and a reduction with hydrogen at elevated temperatures by Komanoya *et al.*<sup>62</sup>



Figure 2 TEM images of a) CMK-3; b-d) Ru/CMK-3

The total amount of acid sites was determined using NH<sub>3</sub>-TPD (Table 3 and Figure 3). A large peak was observed for both samples with a maximum of 435°C (Ru/CMK-3) and 483°C (CMK-3), indicative for the presence of strong acid sites. Ru/CMK-3 also shows weak acid sites as indicated by the peak at 267 °C. This peak is likely due to the presence of Brønsted acidic RuO<sub>2</sub>·2H<sub>2</sub>O sites, as proposed by Komanoya *et al.* <sup>62</sup> As such, the main source for the acid sites is the support, though some additional acidity is generated by oxidized Ru nanoparticles. However, the latter species are likely reduced under reaction conditions by molecular hydrogen and as such likely do not contribute during the actual hydrolysis/hydrogenation reactions.



Figure 3 NH<sub>3</sub>-temperature programmed desorption profiles of CMK-3 and Ru/CMK-3

Table 3 NH<sub>3</sub>-temperature programmed desorption of CMK-3, Ru/CMK-3, spent Ru/CMK-3 and fresh Ru/C

SAMPLE	NH <sub>3</sub> -uptake [μmol/g <sub>cat</sub> ]	τ <sub>d1</sub> <sup>[a]</sup> [°C]	<i>x</i> <sub>1</sub> <sup>[b]</sup>	τ <sub>d2</sub> <sup>[a]</sup> [°C]	<i>x</i> <sub>2</sub> <sup>[b]</sup>
CMK-3	158	-	-	483	1.0
Ru/CMK-3	180	267	0.10	435	0.90
Ru/CMK-3 (spent)	110	223	0.06	392	0.94
Ru/C	122	257	0.12	607	0.88

<sup>a</sup> Temperature of maximum desorption of NH<sub>3</sub>:  $T_{d1}$ , 100-300°C;  $T_{d2}$ , 300-800°C; <sup>b</sup>Fractional population of sites: x<sub>1</sub>, between 100 and 300°C; x<sub>2</sub>, between 300 and 800°C

The acidity value for CMK-3 (158  $\mu$ mol/g<sub>cat</sub>) is in the range for carbon nanotubes activated with nitric acid using various synthetic procedures (120-250  $\mu$ mol/g<sub>cat</sub>). CMK-3 is typically prepared by using SBA-15 silica as the template and sucrose as the carbon source. After sucrose impregnation, the suspension is treated with sulfuric acid, and carbonized at elevated temperatures, followed by SBA-15 removal using a basic treatment. As a result,

CMK-3 has oxygenated functional groups on the surface, examples are carboxylic, lactonic, and phenolic groups<sup>57</sup>. For comparison, the acidity of the commercial Ru/C catalyst was also determined (122  $\mu$ mol/g<sub>cat</sub>) and the values is considerably lower than for Ru/CMK-3 (158  $\mu$ mol/g<sub>cat</sub>), which is likely related to the preparation procedure.

The metal dispersion for both Ru/CMK-3 and Ru/C was determined by H<sub>2</sub> chemisorption measurements (see Table 4 for details). The average particle diameter for the Ru/CMK-3 catalyst was 3.3 nm, in line with TEM data. The dispersion was calculated to be close to 31%. The average Ru particle diameter for the commercial Ru/C catalyst is by far larger (12.4 nm), which is expected to have an effect on catalyst activity (*vide infra*). These findings are in line with the TEM images (Figure S1, supplementary information) that evidenced the presence of Ru clusters containing Ru particles of 5-10 nm in size, together with single Ru particles with a regular spherical form with size ranging from 5 to 50 nm.

Table 4 Catalyst data from H<sub>2</sub> chemisorption measurements

Comple	H <sub>2</sub> uptake	MSA <sup>a</sup>	D	d <sup>b</sup>
Sample	[µmol/g <sub>cat</sub> ]	[m²/g <sub>cat</sub> ]	[%]	[nm]
Ru/C	20.1	2.0	8.1	12.4
Ru/CMK-3	30.2	3.0	30.6	3.3
Ru/CMK-3 (spent)	21.6	2.1	21.8	4.6

<sup>a</sup> Assuming a surface concentration of metal atoms of 1.22·10<sup>19</sup> at/m<sup>2</sup> (from the arithmetic average of planar densities for the three lowest index surface planes), <sup>b</sup> Crystallites diameter assuming a spherical shape of particles

# 3.2 Hydrogenation of levoglucosan using Ru/CMK-3 and Ru/C

The hydrogenation of levoglucosan (LG) in water using Ru/CMK-3 (2 wt.% Ru on support) was investigated as a function of the temperature (120-180 °C) in a batch hydrogenation setup at 50 bar hydrogen pressure for a batch time of 5 h (0.5 M LG, 6 wt.% catalyst on substrate). After reaction, the liquid phase was analysed by HPLC to identify and quantify the main reaction products. The conversion of levoglucosan and the selectivity towards the main products versus the reaction temperature are shown in Figure 4.



Figure 4 Hydrogenation of levoglucosan using Ru/CMK-3 at three temperatures (120-180  $^{\circ}$ C, 5 h, 0.5 M LG, 6 wt.% catalyst on LG)

At 120 °C, the conversion of levoglucosan is limited (3 wt.%), and sorbitol is the main product. Substantial amounts of glucose are also present, indicating that hydrolysis of LG to glucose indeed occurs under the reaction conditions and that glucose is the intermediate product. At 150 °C, the conversion of levoglucosan increased to 31 wt.%. Main products are again sorbitol and glucose. The selectivity to sorbitol increased from 75 to 91 wt.%, indicating that the rate of the hydrogenation reaction is more enhanced at elevated temperatures than the hydrolysis reaction of LG to glucose. Full conversion of levoglucosan is achieved at 180 °C in 5 h, with a sorbitol selectivity as high as 96.2 wt.%, together with 3.8 wt.% of mannitol. The presence of mannitol indicates the occurrence of an isomerization reaction of glucose to fructose or a subsequent isomeriation of sorbitol to mannitol. Possible other by-products, like smaller diols from hydrogenolysis reactions and conversion products from glucose like HMF and levulinic acid, were not observed.

For comparsion, levoglucosan hydrogenations in water using a commercial Ru/C (5 wt.% Ru loading) catalyst were also performed in the temperature range 120-180  $^{\circ}$ C. The conversion of levoglucosan and the product selectivity are shown in Table 5.

Temperature	Conversion,	Sorbitol,	Mannitol,	Glycerol, wt.%	1,2-Propanediol,
	wt.%	wt.%	wt.%		wt.%
120 °C	2.0	100	0	0	0
150 °C	14.7	22.4	0	0	17.3
180 °C	59.7	41.1	8.5	10.3	2.3

Table 5 Results for the catalytic conversion of levoglucosan using Ru/C<sup>a</sup>

<sup>a</sup> 6 wt.% catalyst on substrate, 0.5 M LG in water, 50 bar, 5 h, batch. The mass balance is not closed due to the presence of other unidentified components (HPLC).

It is evident that the Ru/C catalyst is by far less active than Ru/CMK-3, despite the fact that the Ru-loading is 2.5 times higher (2 versus 5 wt.%). At 180°C, the LG conversion was 60 %, compared to close to quantitative conversion for Ru/CMK-3. In addition, the product portfolio differs considerably from that for Ru/CMK-3 and substantial amounts of glycerol and propanediol are formed besides sorbitol and small amounts of mannitol. The presence of the former compounds are indicative for the occurrence of hydrogenolysis reactions, in line with research from Bindwal *et al.* using Ru/C.<sup>55</sup> For Ru/C, glucose was not detected in any of the product samples.

# 3.3 Mechanistic pathways

The proposed mechanistic pathway for the hydrogenation of levoglucosan to C6-polyols is shown in Scheme 2. The desired pathway involves the hydrolysis of levoglucosan to glucose followed by the hydrogenation of glucose to sorbitol. The former is expected to be catalyzed by the acid sites on the catalysts, while the latter is Ru catalysed. However, the formation of C-C splitting products was also observed for Ru/C, indicating the occurrence of catalytic hydrogenolysis reactions of intermediates/products.

To gain insights in the reaction pathways and to identify the differences in performance between Ru/CMK-3 and Ru/C, a number of additional reactions were performed. These involved i) the determination of concentration-time profiles for a number of reactions, allowing calculation of initial rates and turnover frequencies (TOF) and ii) individual reactions with intermediate/products (glucose/sorbitol), both in the presence and absence of hydrogen.



Scheme 2 Proposed reaction pathways for hydrogenation of levoglucosan

Initial experiments involved determination of the initial rate for the catalytic hydrogenation reactions of LG with both Ru/CMK-3 and Ru/C. The initial rates were determined from the slope of the concentration-time profiles for a batch reaction of 5 h with intermediate sampling (see Figures S4 and S5 in the supplementary information). The data are compiled in Table 6.

Table 6 Initial reaction rates and TOF's for levoglucosan and glucose hydrogenation using Ru/CMK-3 and  $Ru/C^a$ 

Entry	Catalysts	Substrate	Initial rate	TOF	TOF	TOF	TOF
			(mmol	(mmol/(g	(mol/mol	(mol/(mol	(mol/(mol
			substrate/h)	cat·h))	acid	Ru	Ru at
					sites.h) <sup>b</sup>	intake∙h) <sup>c</sup>	surface∙h) <sup>d</sup>
1	Ru/CMK-3	Levoglucosan	7.0	34.1	187		
2	Ru/C	Levoglucosan	4.1	20.4	167		
3	Ru/CMK-3	Glucose	98	487		2460	8040
4	Ru/C	Glucose	101	495		1000	12350

<sup>a</sup> 6 wt.% catalyst on substrate, 0.5 M substrate in water, 70 bar total pressure at 180 °C, 5 h, batch, <sup>b</sup> acidity as determined by ammonia-TPD, <sup>c</sup> Total amount of Ru on the catalysts, <sup>d</sup> Ru on the surface of the catalysts as determined by hydrogen chemisorption.

The hydrogenation reaction of LG with Ru/CMK-3 gave sorbitol/mannitol as the main product, with glucose as the intermediate, in line with a consecutive mechanism involving the hydrolysis of LG to glucose followed by hydrogenation to C6-polyols (Scheme 2). For Ru/C, glucose was not detected in significant amounts and sorbitol was the initial product whereas glycerol and 1,2-propanediol were formed after longer batch times. This pattern of reactivity implies that sorbitol is initially formed and subsequently converted to glycerol and 1,2-propanediol (*vide infra*).

The initial rate for the conversion of LG was considerably higher for Ru/CMK-3 (34.1 mmol/g cat·h) than for Ru/C (20.4 mmol/g cat·h). A likely explanation for the higher conversion rate of levoglucosan in the case of Ru/CMK-3 is a higher reaction rate of the acid catalysed hydrolysis of LG to glucose. These findings are in line with the acidity measurements by NH<sub>3</sub>-TPD, showing that Ru/CMK-3 is more acidic in nature than Ru/C. The initial activity, expressed in mol per mol acid sites per h is about equal for both catalyst (167-187 mol/mol acid sites·h, see Table 6), an indication for a first order dependency in acid sites. It is also of interest to note that neither 5-hydroxymethylfurfural (HMF) nor levulinic acid were detected in the reaction mixtures by acid catalysed reactions of glucose (Scheme 2). As such, the rate of hydrogenation of glucose under the prevailing conditions to sorbitol is much faster than the acid catalysed conversions.

The higher activity for the hydrolysis reaction of LG for Ru/CMK-3 was supported by performing experiments with Ru/CMK-3 and Ru/C using LG in the presence of the catalyst but by replacement of the hydrogen atmosphere by an inert  $N_2$  atmosphere. The results are compiled in Table 7 and show a much higher conversion rate for Ru/CMK-3, confirming its higher acidity.

Table 7 Hydroly	sis reactions o	of levoglucosan	using Ru/	CMK-3 and Ru/	Ca
				•	

Entry	Catalysts	Conversion of levoglucosan, wt.%	Selectivity to glucose, wt.%
1	Ru/CMK-3	98.2	34.0
2	Ru/C	64.9	54.9

<sup>a</sup> 6 wt.% catalyst on substrate, 0.5 M LG in water, 50 bar  $N_2$ , 180 °C, 5 h, batch

The performance of the catalysts for the hydrogenation of the intermediate glucose was also tested independently by performing hydrogenation reactions with glucose in a batch set-up

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for both catalysts with product sampling at various batch times. The results are given in Table 6, the individual concentration profiles are given in the supplementary information (Figures S6-S7). For both catalyst, glucose is converted quantitatively within about 1 h. The initial activity for both catalyst is about equal (490 mmol/(g cat·h)). When compensating for the differences in Ru loading (2 wt.% for Ru/CMK-3 versus 5 wt.% for Ru/C), the Ru/CMK-3 catalyst is more active (2460 versus 1000 mol/mol Ru intake h). This difference in activity is mainly due to the differences in the average Ru nanoparticle sizes according to  $H_2$ chemisorption and supported by TEM, which were shown to be larger for Ru/C than for Ru/CMK-3. When considering the activity on the amount of Ru sites on the surface of the nanoparticles, the activity of the Ru/C is actually higher than for Ru/CMK-3 (Table 6). Of interest is the product portfolio for both catalyst and particularly the evolution of intermediates/products in time. It is evident that sorbitol is the main product. However, particularly for Ru/C, the amount of sorbitol shows a maximum and after a certain batch time, considerable amounts of glycerol are formed (Figure S6, supporting information). This indicates that sorbitol is, particularly for Ru/C, not inert under the given reaction conditions and reacts further to smaller polyols by hydrogenolysis reactions, lowering the selectivity to the desired sorbitol.

Further proof that C3 products are indeed formed from sorbitol was obtained by performing batch experiments with sorbitol as the substrate at 180°C with both Ru/CMK-3 and Ru/C as the catalyst (Table 8). Indeed, sorbitol is not inert under these conditions, though conversions were below 22 %. In addition, Ru/C was by far more reactive than Ru/CMK-3. The main products were mannitol and hydrogenolysis products. These findings indicate that sorbitol is the source for the smaller polyols like glycerol. In addition, it also suggests that sorbitol may be isomerized to mannitol by the Ru catalyst, in line with literature data<sup>63</sup>.

Table 8 Sorbitol hydrogenolysis using Ru/C and Ru/CMK-3<sup>a</sup>

Catalysts	Reaction	Sorbitol Conversion,	Mannitol Selectivity,	Glycerol Selectivity,
	time, h	wt.%	wt.%	wt.%
Ru/C	5	21.5	39.1	60.9
Ru/CMK-3	5	9.8	35.6	64.4

 $^{a}$  6 wt.% catalyst on substrate, 0.5 M sorbitol in water, 50 bar, 180  $^{\circ}$ C, 5 h, batch

Thus, from the data above, we can conclude that sorbitol is formed from LG by a two step hydrolysis-hydrogenation sequence. However, the sorbitol is not inert under the conditions applied and may be converted to smaller polyols, the result of C-C scission products by hydrogenolysis. Hydrogenolysis reactivity is by far more pronounced for Ru/C than Ru/CMK-3 and this is the explanation for the superior perfromance of Ru/CMK-3 in the reaction of LG to C6-polyols. So far, we do not have a convincing explanation for this difference in reactivity between Ru/CMK-3 and Ru/C for the hydrogenolysis reaction. Recently, Triantafyllidis *et al.*<sup>8</sup> reported experimental work on the hydrogenation of glucose to sorbitol using Ru on activated carbon (Norit, SAE, SUPER) and showed that the amount of byproducts from hydrogenolysis of sorbitol was considerable (7-45%) and a function of process conditions, metal loading and catalyst reduction procedure (H<sub>2</sub> versus NaBH<sub>4</sub>). XPS and HRTEM measurements for both types of activated catalysts showed a difference in the amounts of zerovalent (crystalline) and charged Ru (non-crystalline) nanoparticles and this was put forward as an explanation for the differences in the rate of hydrogenolysis of sorbitol for the various catalysts.

# **3.4 Catalyst stability**

To gain insights in the stability of the Ru/CMK-3 catalyst, recycling studies for levoglucosan hydrogenation were carried out and the results are given in Figure 5. After 3 successive runs at 180 °C for 3 h batch times, around 92 wt.% of levoglucosan conversion was observed for all the 3 runs. However, the selectivity to sorbitol decreased from 94 to 88 wt.% whereas glucose selectivity increased from 2 to 7 wt.%. As such it implies that the acid sites on Ru/CMK-3 necessary for the hydrolysis of LG are largely preserved under the selected reaction condition, while the hydrogenation activity of Ru/CMK-3 slightly decreased.



Figure 5 Recycling tests for Ru/CMK-3 for levoglucosan hydrogenation (5 h, 0.5 M LG, 6 wt.% catalyst on LG)

The spent Ru/CMK-3 catalyst after 1<sup>st</sup> run was characterized by TEM (Figure 6), ammonia-TPD (Table 3) and hydrogen chemisorption (Table 4). The textural appearance as determined by TEM showed strong resemblance with the fresh sample. Ammonia TPD measurements indicated that the acidity is slightly reduced after an experiment, whereas the mean diameter of the Ru nanoparticles increased slightly (from 3.3 to 4.6 nm, H<sub>2</sub> chemisorption data, see Table 4). As such, the observed reduction in hydrogenation activity after one recycle is likely due to a slight increase in the Ru nanoparticle size.



Figure 6 TEM images of spent Ru/CMK-3

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# 3.5 Hydrogenation of disaccharides using Ru/CMK-3

To extend the scope for the use of Ru/CMK-3 for combined hydrolysis-hydrogenation reactions, the catalyst was also tested for two sugar oligomers, cellobiose and sucrose. Cellobiose is the simplest sugar oligomers containing a 1, 4- $\beta$ -glucoside bond connecting two glucose monomers. In sucrose, glucose and fructose are linked via an ether bond between C1 on the glucosyl unit and C2 on the fructosyl unit. The results for the conversion of cellobiose and sucrose and the product selectivity using Ru/CMK-3 in water at 180 °C for 5 h are shown in Table 9.

Table 9 Conversion and product selectivity for the hydrogenation of disaccharides using Ru/CMK- $3^{a}$ 

Substrate	Conversion,	Sorbitol,	Mannitol,	Others,	Total C6 alcohols,
	wt. %	wt.%	wt.%	wt.%	wt.%
Cellobiose	100	91.1	4.5	4.4	95.6
Sucrose	100	61.6	36.3	2.1	97.9

<sup>a</sup> 6 wt.% catalyst on substrate, 0.25 M of disaccharides in water, 50 bar, 5 h, batch, 180°C

Full conversion was observed for both substrates after a reaction of 5 h at 180 °C. In the case of cellobiose, the total sugar alcohol yield was 95.6 % with 91.1 % of sorbitol and 4.5 % of mannitol (HPLC). Mannitol is known to be formed by the hydrogenation of fructose, the isomerization product of glucose. Glucose was not detected in any of the product mixtures.

Two reaction pathways can be envisaged for the reaction, *viz* i) a hydrolysis-hydrogenation pathway involving hydrolysis of the 1,4- $\beta$ -glucoside bond of cellobiose forming glucose, which is further hydrogenated to sorbitol or ii) an initial hydrogenation of the reducing sugar end to cellobitol (3- $\beta$ -D-glucopyranosyl-D-glucitol) followed by hydrolysis to sorbitol and glucose and a second hydrogenation (see Scheme 3).

Recent kinetic studies by Palkovits *et al.*<sup>64</sup> on cellobiose and trisaccharides using Ru/C in combination with a heteropoly acid showed that the latter pathway is taking place to a large extent. The hydrogenation followed by hydrolysis sequence was shown to be preferred at low reaction temperatures and for longer oligomers. Similar findings were reported by Wang *et al.* <sup>56</sup> for bifunctional Ru catalysts supported on Ru/Cs<sub>2</sub>HPW<sub>12</sub>O<sub>40</sub>.



Scheme 3 Proposed reaction pathways for hydrogenation of cellobiose over Ru/CMK-3 catalyst

In the product mixtures of the experiments reported in Table 9, cellobiotol, was not observed, likely due to the long reaction time of 5 h. A number of experiments was performed using cellobiose as the starting material at shorter reaction times and the results are provided in Figure 7. Indeed, after 0.5 h, significant amounts of cellobitol (41 % selectivity) were present in the reaction mixture, beside only minor amounts of glucose. In addition, all cellobiose was quantitative converted after 30 min. As such, reaction pathway ii) (hydrogenation followed by hydrolysis) seems to be favored with the Ru/CMK-3 catalyst under these conditions.



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Figure 7 Product composition versus time for the hydrogenation of cellobiose using Ru/CMK-3 (180 °C, 0.25 M cellobiose, 6 wt.% catalyst on cellobiose)

Catalytic cellobiose hydrogenations have been reported in the literature and the results for Ru based catalysts<sup>56, 65-67</sup>, of relevance for this paper, are summarized in Table 10. Best results with quantitative sorbitol yield at 100 % cellobiose conversion were obtained using Ru nanoparticles in combination with a Brønsted acid (HCl) at 120°C, 40 bar hydrogen and a batch time of 12 h<sup>65</sup>. For bifunctional hydrolysis-hydrogenation catalyst, the best sorbitol yield was 93 wt.%<sup>56</sup> (Table 10, entries 8-10) using a Ru/Cs<sub>2</sub>HPW<sub>12</sub>O<sub>40</sub> catalyst. As such, the performance of the Ru/CMK-3 catalyst is about similar to the best bifunctional catalyst reported to date for the conversion of cellobiose to sorbitol.

Entry	Substrate	Temperature	H <sub>2</sub>	Reaction time	Catalysts	Conversion (mol.%)	Product selectivity (mol.%)	Ref.
1	Cellobiose	120 °C	40 bar	12 h	Ru/C	100 %	>99 % of cellobitol	65
2	Cellobiose	120 °C	40 bar	12 h	Ru nanoparticles with	100 %	100 % of sorbitol	65
					HCI (pH=2)			
3	Cellobiose	120 °C	40 bar	12 h	Ru nanoparticles,	87.8 %	64.8 % of cellobitol, 26.4 % of sorbitol,	65
					pH=7		1.6 % of glucose, 7.2 % of polyols	
4	Cellobiose	120 °C	40 bar	12 h	Ru nanoparticles,	75.6 %	55.7 % of cellobitol, 24.0 % of sorbitol,	65
					with NaOH (pH=10)		3.2 % of glucose, 17.1 % of polyols	
5	Cellobiose	160 °C	50 bar	2 h	Ru/C	100 %	99 % of cellobitol	66
6	Cellobiose	120 °C	50 bar	1.8 h	Ru/C + silicotungstic	83 %	81 % of cellobitol, 18 % of sorbitol,	66
					acid		trace amount of glucose	
7	Cellobiose	170 °C	50 bar	1.25 h	Ru/C + silicotungstic	100 %	<1 % of cellobitol, 75 % of sorbitol,	66
					acid		trace amount of glucose	
8	Cellobiose	140 °C	20 bar	6 h	$Ru/Cs_2HPW_{12}O_{40}$	100 %	trace amount of cellobitol, 93 % of sorbitol	56
9	Cellobiose	140 °C	20 bar	6 h	$Ru/Cs_3PW_{12}O_{40}$	100 %	10 % of cellobitol, 86 % of sorbitol	56
10	Cellobiose	180 °C	50 bar	3 h	Ru/CNT	100 %	5 % of cellobitol, 88 % of sorbitol, 2 % of	67
							mannitol	

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In the case of sucrose, quantitative conversion was observed after 5 h at 180°C, with a C6 sugar alcohol selectivity of close to 98 %. The major difference when comparing with the results for cellobiose is the sorbitol to mannitol ratio, and for sucrose, the mannitol yield is as high as 36.3 wt.%. This may be explained by considering that the hydrogenation of fructose is known to give mannitol and sorbitol in a close to one to one ratio, while hydrogenation of glucose gives mainly sorbitol with trace amounts of mannitol (*vide supra*). Literature precedents for the hydrogenation of sucrose to C6-sugar alcohols in a single step are rare.<sup>68</sup> In most cases, sucrose is first hydrolysed to glucose and fructose and then hydrogenated In a second step.<sup>69</sup> Thus, the concept of the use of a bifunctional Ru/CMK-3 catalyst for disaccharides also is highly successful for sucrose.

# Conclusions

C6-sugar alcohols and particularly sorbitol are attainable from LG in excellent yields (> 96%) using a mesoporous carbon supported Ru/CMK-3 as the catalyst and water as the solvent. Catalyst performance is superior to Ru/C, for which significant amounts of smaller diols were obtained, indicative for the occurrence of hydrogenolysis reactions leading to C-C bond cleavage. The excellent performance of the Ru/CMK-3 catalyst, both in terms of activity and selectivity, is due to the low rate of subsequent hydrogenolysis reactions of sorbitol to smaller polyols, as was shown by separate reactions with sorbitol. The bifunctional character of the catalyst (hydrolysis/hydrogenation capabilities) was also shown for the hydrolysis-hydrogenation of disaccharides (cellobiose and surcose), again giving excellent yields of C6 sugar alcohols. In addition, recycling studies in batch with LG as the starting material reveal a small reduction in the rate of glucose hydrogenation for 3 successive runs, rationalised by a slight increase in the Ru nanoparticle size (TEM, H<sub>2</sub> chemisorption). These findings indicate that Ru/CMK-3 is a potentially very attractive catalyst for the conversion of sugar fractions of pyrolysis liquids, known to contain considerable amounts of LG and cellobiose, to sugar alcohols. These studies are in progress and will be reported in due course.

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# **Supporting Information**

TEM images of the Ru/C catalyst,  $N_2$  adsorption isotherms, pore size distributions of CMK-3 and the Ru analogue and concentration-time profiles of LG and glucose hydrogenation using Ru/CMK-3 and Ru/C.

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# Graphical Abstract for TOC



Ru/CMK-3