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Hydrogenation of fructose on Ru/C catalysts

Annemieke W. Heinen, Joop A. Peters *, Herman van Bekkum

Laboratory of Applied Organic Chemistry, Delft University of Technology, Julianalaan 136, NL-2628 BL Delft, The Netherlands

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Abstract

The hydrogenation of D-fructose on Ru/C catalysts was studied. Under the conditions applied (1 bar H_2, 72 °C), the furanose forms of D-fructose react, while the pyranose forms do not. However, all anomers adsorb with comparable strength on the surface. The reaction rate is controlled by product inhibition. The selectivity to D-mannitol can be increased from 47 to 63% by promotion of Pd/C and Pt/C catalysts with Sn.

Keywords: Activated carbon; Tin, promoter; D-Mannitol; D-Glucitol

1. Introduction

The hydrogenation of D-fructose (see Scheme 1) is an interesting reaction in view of the production of the low-caloric sweetener D-mannitol [1]. D-Mannitol can be obtained from the relatively expensive sources D-fructose and D-mannose in yields of about 45 and 100%, respectively. This explains the price difference: $3.32/pound for D-mannitol and $0.75/pound for D-glucitol (US market) [2]. When applying an isomerization catalyst (glucose isomerase) in combination with a hydrogenation catalyst (e.g., supported copper) D-glucose can also serve as starting compound for D-mannitol [3,4]. For economical reasons D-mannitol is prepared by hydrogenation of a 1:1 mixture of D-glucose and D-fructose, obtained by hydrolysis of sucrose. In this way a mixture of about 70% D-glucitol (sorbitol) and 30% D-mannitol is obtained, from which D-mannitol can be isolated by crystallisation. By contrast, D-glucitol is prepared by hydrogenation of inexpensive D-glucose with 100% selectivity.

There is growing interest in the production of D-mannitol from D-fructose due to the increasing production of inulin. Inulin is an oligosaccharide consisting of (2→1)-linked β-D-fructofuranosyl units attached to a D-glucose end group. Inulin is a potentially attractive feedstock for the production of D-mannitol due to its high fructose-to-glucose ratio. This study focuses on the hydrogenation of fructose.

Noble metals, preferably supported on activated carbon, are frequently used catalysts for carbohydrate conversions [5]. Activated carbon is cheap, has a high surface area and is resistant to both strongly acidic and strongly basic media. Another advantage is the easy recovery of the precious metal from the catalyst by burning off the carbon support. However, due to the fact that carbon originates from natural products, like for instance peat or wood, every batch of activated carbon can

* Corresponding author. Tel.: +31-15-2785892; fax: +31-152-784289.

E-mail address: j.a.peters@tnw.tudelft.nl (J.A. Peters).

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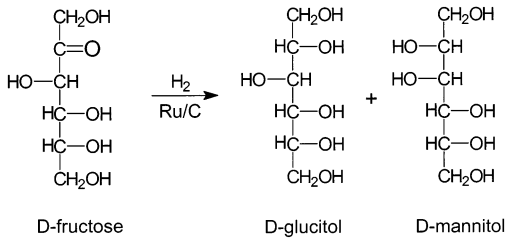


Scheme 1. Hydrogenation of D-fructose to D-glucitol and D-mannitol. D-Fructose is presented in its open form, which represents just 3% of the mutarotation equilibrium in water at 80 °C.

have different properties. These differences can have large influences on the performance of the catalyst.

Ruthenium is the most active catalyst in carbohydrate hydrogenations, both in homogeneous [6,7] and in heterogeneous catalysis [8]. This paper describes a study on the hydrogenation of D-fructose using Ru/C catalysts. Besides the kinetics of this reaction and an investigation of the reacting tautomeric forms, the effect of different carbon supports and impregnation solvents on the activity and selectivity of these catalysts is presented. Furthermore, the effect of tin promotion on the selectivity to D-mannitol is investigated.

2. Results and discussion

Catalyst characterization.—The amount of acidic oxygen sites (mainly carboxylic groups) on the carbon was increased by treatment with nitric acid. Titration of the oxidized carbon SX1GN65 (see experimental) with sodium hydroxide showed the presence of 1.0 meq g^{-1} of acid sites, compared with 0.1 meq g^{-1} for the untreated carbon. The intensity of the 1700 cm^{-1} band in the IR spectrum, relative to the band at 1580 cm^{-1} is also an indication of the amount of carboxylic groups. For the untreated carbon, the relative intensity of the 1700 cm^{-1} band was 0, whereas for the HNO_3 treated carbon this value amounted to 0.38. In addition to the increased acidity, the carbon had a more hydrophilic surface by this treatment, as was shown previously by means of competitive adsorption of water and toluene [9].

Carbon monoxide adsorption measurements, X-ray fluorescence spectroscopy (XRF) and transmission electron microscopy (TEM) analyses were performed on the Ru/C catalysts. The XRF and CO data are displayed in Table 1. These data show that the Ru content of SX1G, impregnated with aqueous $RuCl_3$, is somewhat lower than that of the other catalysts, probably due to the smaller amount of anchoring groups on the surface and the limited wettability of the surface by water. The CO adsorption of these catalysts is, however, comparable with the other ones. An Ru dispersion of 77%, assuming 100% linear CO adsorption, is the highest of all catalysts.

A TEM study was performed on these catalysts. On Ru/SX1G impregnated with aqueous $RuCl_3$ and reduced in 10% H_2/N_2, metal particles could not be clearly discerned, although Ru was clearly detected using EDX elemental analysis. Therefore, the metal must be present as very small (< 0.5 nm) particles. The same observations were made after use of this catalyst in a hydrogenation experiment. Since the atomic radius of Ru is 0.134 nm [10], this means that the metal is present as clusters of only a few atoms.

Reduction of the same catalyst-precursor in 100% H_2 gave a catalyst with mainly small particles of around 0.5 nm, besides a few of a somewhat larger size (1–1.5 nm). The catalyst impregnated with ethanolic $RuCl_3$ showed

Table 1
CO adsorption results of the Ru/C catalysts prepared on different carbons and with different solvents

Catalyst	Ru content (wt%)	CO adsorbed (mL g^{-1})	CO/Ru
Ru/SX1G (acetone) 10% H_2	3.50 ($\pm$0.11)	5.0	0.59
Ru/SX1G (water) 10% H_2	2.82 ($\pm$0.09)	5.1	0.75
Ru/SX1G (water) 100% H_2	2.82 ($\pm$0.09)	5.2	0.77
Ru/Darco (water) 10% H_2	3.47 ($\pm$0.11)	4.0	0.47
'5 wt% Ru/C', Acros	3.35 ($\pm$0.11)	5.7	0.69

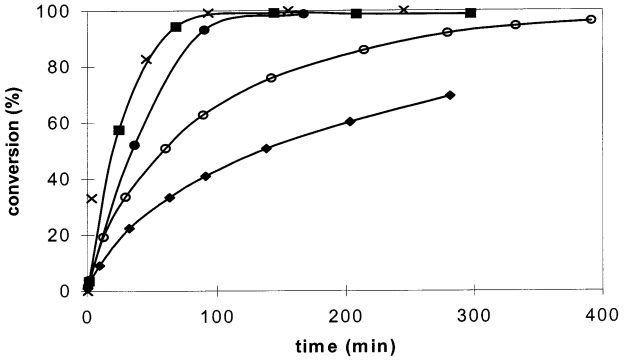


Fig. 1. Conversion of D-fructose against time in the hydrogenation of D-fructose over 0.05 g Ru/C (Acros) at 100 °C and 100 bar H_2 (×); 100 °C, 30 bar (■); 60 °C, 30 bar (●); 72 °C, 1 bar (○); 38 °C, 1 bar (◆); 1 g D-fructose, 80 mL water.

Table 2
Reaction rate of D-fructose hydrogenation at different D-fructose starting concentrations; 0.05 g Ru/C (Acros), 80 mL water, 72 °C, 1 bar H_2

[F] (mol L^{-1})	Fructose (g)	r_0 (mol L^{-1} h^{-1})
0.034	0.5	0.047
0.069 (standard experiment)	1.0	0.033
0.139	2.0	0.033
0.347	5.0	0.035
1.656	24.0	0.030

small particles of 0.5–1 nm, just visible with this technique. Impregnation with an acetone solution resulted in a high Ru signal with EDX analysis, although Ru particles were not observed. This indicates the presence of Ru particles with a size below the detection limit. The catalysts based on Darco and SX1GN65 showed somewhat larger particles. The particles on Ru/Darco range from 1 to 1.5 nm, with, according to EDX, smaller particles in between; on SX1GN65 small particles (0.5–2 nm) were observed, besides a few clusters up to 20 nm. The same observations were made for the commercial Ru/C catalyst.

Comparing the TEM results with the CO adsorption data of Table 1, we can conclude that the trends observed with TEM are in agreement with the results of the adsorption data.

Kinetics of fructose hydrogenation.—Hydrogenations of carbohydrates are usually carried out under high pressure. Typical reaction conditions for D-glucose (batch) hydrogenation are 70–140 bar and 120–160 °C [11]. In continuous hydrogenation, higher pressures (up to 180 bar) are applied. The effect of temperature and pressure on the conversion of D-fructose over the commercial 5 wt% Ru/C is shown in Fig. 1. The order in H_2 is about zero and even at 1 bar a high activity is obtained. Therefore, the reaction was further studied under 1 bar H_2 pressure and at 72 °C.

The reaction was 100% selective to the two alditols, i.e., no side product was formed. The selectivity to D-mannitol over this catalyst varied from 40% (100 °C, 100 bar) to 43% (72 °C, 1 bar) in the reactions over Ru described here.

The system was checked for external transport limitation by varying the catalyst concentration and the impeller speed. A linear relationship between the initial rate constant and the amount of catalyst was observed, which indicates that the reaction is first order in catalyst concentration. This, together with the fact that there is no influence of the stirring speed ($\text{at} \geq 1000$ rpm) on the activity, shows that external diffusion is not rate controlling. With the Ru dispersion displayed in Table 1 (assuming 100% linear CO adsorption, i.e., $CO{:}Ru_{exposed} = 1{:}1$), the turnover number (TON) amounts to 483.

A plot of ln [D-fructose] against time gives a straight line (with a correlation coefficient of 0.9980), suggesting first order kinetics in D-fructose. However, upon increasing or decreasing the initial D-fructose concentration, the initial reaction rate does not change accordingly (Table 2). The selectivity, however, was independent of the D-fructose starting concentration. Even at a concentration as high as 30 wt% of D-fructose, the selectivity to mannitol amounted to 43%.

The reaction was checked for product inhibition by addition of D-glucitol and/or D-mannitol to the reaction mixture (Fig. 2). This Figure indicates a competition between D-fructose and the reaction products for adsorption on the catalyst.

The results displayed in Fig. 2 can be explained using Langmuir–Hinshelwood kinetics [12,13]. According to the following reaction (where * presents an empty reaction site):

$$\text{fructose (aq)} + * \overset{b_f}{\rightleftharpoons} \text{fructose (adsorbed)}$$

$$\overset{k}{\rightarrow} \text{mannitol} + \text{glucitol}$$

the reaction rate will be proportional to the D-fructose surface coverage θ_f:

$$r = -\mathrm{d[F]}/\mathrm{d}t = k\theta_f$$

The adsorption coefficients b_f an b_{H2} are defined as:

$$b_f = \theta_f / c_f \theta_*$$

$$b_{H2} = \theta_{H2}^2 / (p_{H2}\theta_*^2)$$

During the hydrogenation, the surface coverage of D-fructose is given by:

$$\theta_f = b_f c_f / (b_f c_f + b_p c_p + \sqrt{(b_{H2} p_{H2})} + b_s c_s + 1)$$

In this equation, the subscripts f, H2, s and p denote D-fructose, hydrogen, solvent and products, respectively. Neglecting the adsorption of the solvent and upon working under a constant hydrogen pressure, a constant value

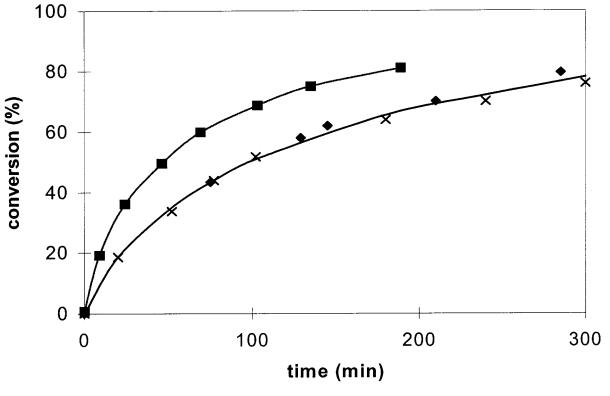


Fig. 2. Hydrogenation of D-fructose over Ru/C (Acros) with different starting mixtures; 1 g D-fructose (■), 1 g D-fructose + 0.5 g D-mannitol + 0.5 g D-gluctitol (×); 1 g D-fructose + 1 g D-glucitol (◆); 0.050 g 5 wt% Ru/C (Acros), 80 mL aqueous solutions, 72 °C, 1 bar H_2.

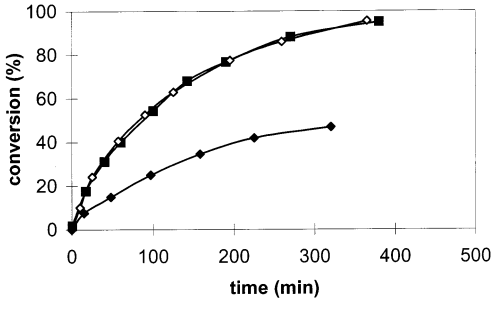


Fig. 3. First (■) use of Ru/C (Acros) and re-use after washing with cold water (◆) and refluxing water (◇); 1 g D-fructose, 0.050 g catalyst, 80 mL water, 72 °C, 1 bar H_2.

C can be introduced, which reduces the rate expression to:

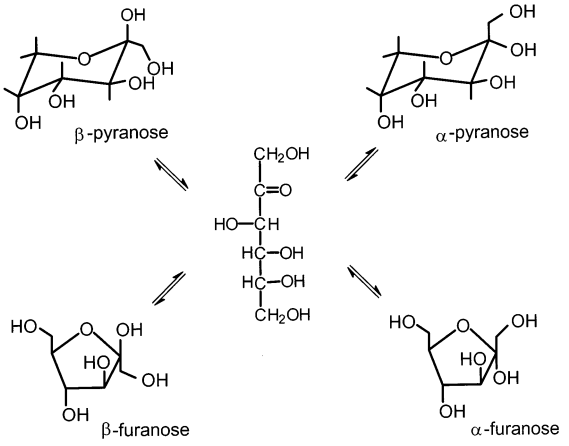
$$r = k b_f c_f / (b_f c_f + b_p c_p + C)$$

This model explains the gradually decreasing rate that was observed during the hydrogenation experiments (see Fig. 2). As Table 2 shows, the reaction rate is independent of the D-fructose starting concentration. The model is only in line with this observation if the constant C can be neglected. Furthermore, the pseudo first-order kinetics that were observed during the experiments indicate that b_p and b_f must be of the same order of magnitude. With curve fitting, a good correlation was obtained when $b_f/b_p \approx 2$ and $k = 0.049\ \mathrm{h}^{-1}$.

Re-use of the catalyst.—Upon re-use of the catalyst after washing with cold water, the activity dropped considerably (Fig. 3). However, after refluxing in water for a night, the filtered and dried catalyst regained its original activity. This indicates the presence of strongly adsorbing species on the catalyst surface after reaction. The ^{1}H NMR spectrum of the filtrate showed that, besides D-fructose, D-mannitol and D-glucitol, a mixture of other polyhydroxy compounds was present. With this method, we were not able to identify these species. The concentrations were too low to be analyzed with ^{13}C NMR.

The catalyst was checked for leaching of ruthenium. AAS measurements indicated 0.575 μg Ru to be present in the reaction solution (80 mL), which corresponds with a 0.03% loss of Ru from the catalyst surface. This small amount of Ru was checked for its catalytic activity by re-use of the reaction mixture filtrate. No conversion of D-fructose occurred in the absence of Ru/C.

Reactivity of the tautomeric forms.—In solution, D-fructose is present in the mutarotation forms presented in Scheme 2. At 80 °C, a D-fructose solution contains 53% β-fructopyranose, 2% α-fructopyranose, 32% β-fructofuranose, 10% α-fructofuranose and 3% open keto-form [14]. The rate limiting step in the mutarotation is the conversion of β-fructopyranose into the keto form. The interconversion between the furanose species is much faster. Flood et al. [15] have reported that the



Scheme 2. D-Fructose mutarotation.

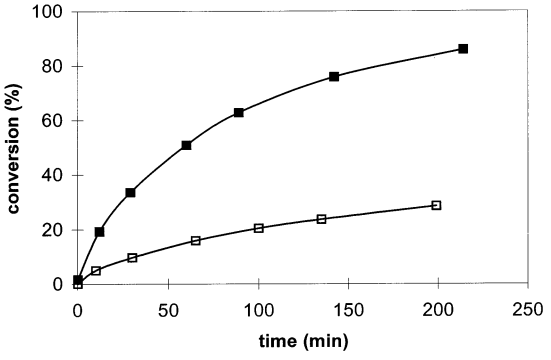


Fig. 4. Effect of D-glucose on the hydrogenation of D-fructose; 1 g D-fructose (■), 1 g D-fructose + 1 g D-glucose (□); 0.050 g Ru/C (Acros), 80 mL aqueous solution, 72 °C, 1 bar H_2.

mutarotation rate constant in water at 70 °C amounts to around 1.3 min^{-1}. In our standard experiment with 0.069 mol L^{-1} D-fructose, the mutarotation rate will, therefore, be around 2.4 mol L^{-1} h^{-1}, which is much faster than the rate of hydrogenation (see Table 2). Interconversion between the different D-fructose species will therefore not be rate limiting.

These tautomeric forms will all have different adsorptivities on the catalyst surface and their own characteristic rates of hydrogenation. Ruddlesden et al. [16] and Makkee et al. [8] showed that hydrogenation over Cu and Ni catalysts occurs by hydrogenation of the ring forms and not by hydrogenation of the acyclic form. The furanose forms were found to be more reactive than the pyranose forms.

Upon addition of D-glucose to the reaction mixture ($c_g^0 = c_f^0$), we observed strong inhibition (Fig. 4). At 31 °C, D-glucose is more than 99% present in the pyranose forms (38% α-, 62% β-pyranose). D-Glucose does not react under the mild conditions applied (70 °C, 1 bar), but apparently the D-glucose tautomeric forms adsorb stronger on the catalyst than the D-fructose forms. Strong D-glucose adsorption and lower reactivity was also observed in the hydrogenation of D-glucose/D-fructose mixtures over a SiO_2 supported copper catalyst [8].

Fig. 5(a) compares the hydrogenation rates of isomaltulose, 6-*O*-(α-D-glucopyranosyl)-D-fructose, and D-fructose. The D-fructose units in isomaltulose (Scheme 3) react with the same rate as D-fructose, both with 0.034 and 0.069 M substrate.

Isomaltulose can adsorb via the D-fructose and via the glucoside unit. The adsorption strength of the α-glucopyranoside unit can be determined from competition experiments with both D-fructose and methyl α-D-glucopyranoside. Fig. 5(b) indicates inhibition of D-fructose hydrogenation by methyl glucoside, resulting in a decrease in rate by a factor of

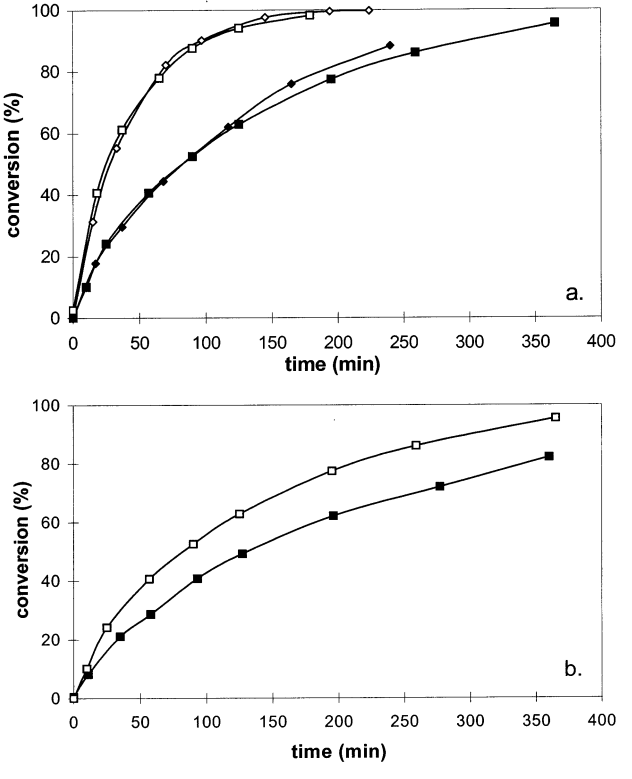
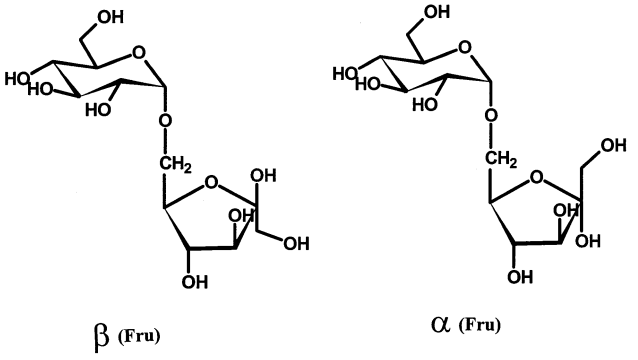


Fig. 5. (a) Hydrogenation of D-fructose (■/□) and isomaltulose (◆/◇), solid symbols: 0.069 M substrate; open symbols: 0.034 M substrate; (b) hydrogenation of 0.069 M D-fructose with (■) and without (□) 0.069 M methyl α-D-glucopyranoside present. 0.050 g Ru/C (Acros), 80 mL aqueous solution, 72 °C, 1 bar H_2.



Scheme 3. The two forms of isomaltulose.

Table 3
Initial reaction rate (r_0) of D-fructose hydrogenation on different Ru/C catalysts reduced for 2 h at 400 °C in 20% H_2/N_2; 1 g D-fructose, 0.05 g Ru/C, 80 mL water, 72 °C, 1 bar H_2

Catalyst	r_0 (mol L^{-1} h^{-1})
Ru/Darco (water)	0.031
Ru/SX1G (water)	0.033
Ru/SX1G (ethanol)	0.038
Ru/SX1G (acetone)	0.067
Ru/SX1GN65 (water)	0.067
Ru/C (Acros)	0.033

two. Therefore, the adsorption strength of the glucoside unit of isomaltulose is comparable with that of the fructofuranoside unit, which means that only half of the available Ru surface is used for adsorption of reactive species.

The equal hydrogenation rates of isomaltulose and D-fructose are a strong indication that on Ru/C one or both furanose forms are the reactive species of D-fructose. The pyranose form (about 50% of the total concentration) adsorbs with equal strength, without reacting. To maintain the furanose/pyranose ratio around 1, the mutarotation rate of the D-fructose must be higher than the hydrogenation rate.

Effect of catalyst preparation method.—Table 3 shows the effect of the carbon support, the impregnation solvent and the reduction method on the hydrogenation activity. Since the rate of the reaction increases linearly with the catalyst concentration, the reaction rate will depend on the Ru surface available for adsorption.

Although the ruthenium surface available for CO is equal for most of the catalysts (see Table 1), the initial reaction rate on Ru/SX1G impregnated with acetone, and Ru/SX1GN65 impregnated with water is twice as high than on the other catalysts. Impregnation of SX1G with ethanol also leads to some increase in the activity, which indicates an effect of the solvent–support interaction.

The results are in line with the observations of Machek et al. [17]. These authors studied the effect of the support-solvent interaction on the Pt distribution and particle size. On activated carbon, better metal distributions and smaller Pt particles were obtained by using more hydrophobic solvents. In fact, the Pt particle size on carbon decreased in the order water > ethanol > acetone. For hydrophilic supports, like alumina, polar solvents resulted in higher dispersions. Using a solvent with a low affinity for the support, the metal particles will be non-uniformly distributed through the pore system.

The data of Table 3 suggest that low solvent–support interactions lead to less active catalysts. The selectivity did not change. Comparison of these results with the CO adsorption data indicates that part of the Ru of these catalysts is not accessible to D-fructose. Therefore, the performance of the catalyst can be influenced by the catalyst preparation method. The type of carbon support, however, does not directly influence the hydrogenation rate.

Sn promotion.—A favourable effect of Sn on the activity of Ru catalysts in the hydrogenation of carbonyl bonds is frequently observed and explained by Sn mediated activation of the C=O bond, facilitating the hydrogen transfer from adjacent Ru sites. Upon hydrogenation of unsaturated carbonyl compounds, this results in a selectivity change towards the unsaturated alcohol [18–21].

Although D-fructose is not hydrogenated via the open keto form, the effect of Sn promotion on the selectivity and activity in this reaction was studied (Table 4). The effect of promotion with Bi is also displayed. Sn was able to increase the selectivity to D-mannitol. With SnPd/C and SnPt/C (2 wt% Sn and 2.5 wt% noble metal) selectivities above 60% were obtained. The selectivity in this reaction is independent of the conversion. The increase in selectivity after promotion of Ru/C was less than on SnPt/C and SnPd/C. Furthermore,

for Ru and Pd the activity decreased dramatically. Lower Sn loadings (up to 0.2 wt%) resulted in higher activities, but in loss of selectivity.

XRD of the SnPd/C and SnPt/C catalysts showed only diffraction patterns of Pd and Pt, respectively; SnRu/C also showed SnO diffraction patterns. To ascertain whether the action of tin is entirely heterogeneous, the Sn concentration in the reaction mixture was measured with AAS. It appeared that 0.8% of the total amount of Sn present on the SnPt/C catalyst was dissolved. The influence of Sn^{4+} and Sn^{2+} ions on the selectivity was checked by addition of 7 mg of $SnCl_4$ and $SnCl_2$, respectively, to the reaction mixture before hydrogenation with Ru/C. The catalyst readily deactivated, suggesting precipitation of Sn species on the Ru surface. Only 36% selectivity to D-mannitol was obtained. It is, therefore, not likely that the selectivity increase is due to homogeneous tin ions in solution.

These results suggest that Ru is covered by Sn species using this preparation technique. A detailed study of the preparation of Sn-promoted Ru/C catalysts in relation to the D-mannitol selectivity is therefore recommended.

Hydrogenation of L-sorbose, which leads to D-glucitol and L-iditol, results in a similar selectivity effect upon promotion of the Pt/C catalyst with tin: the selectivity to D-glucitol increased from 48 to 63%. The selectivity of the isomaltulose hydrogenation, however, was not affected by Sn.

In the hydrogenation of D-fructose, selectivities to D-mannitol over 60% were already reported on Cu/SiO_2 catalysts [8]. This effect was explained by coordination of the furanose forms to the surface and attack of a hydride like species with inversion of configuration. In this way, hydrogenation of the α form leads to D-glucitol, the β isomer gives D-mannitol. In contrast with this Cu catalyst, our Sn promoted catalysts do not affect the selectivity in the hydrogenation of isomaltulose. Perhaps with this catalyst and under these conditions, the pyranose form of D-fructose is one of the reacting species which can coordinate to Sn in such a way that formation of one of the isomers is preferred. However, more insight into tin–fructose coordination is required.

Table 4
Effect of promoters (1 wt%) on the conversion of D-fructose and selectivity to D-mannitol after 20 h of reaction; 1 g D-fructose, 80 mL water, 0.050 g catalyst, 100 °C, 100 bar H_2

Catalyst	Conversion (%)	Selectivity D-mannitol (%)
Ru/C	100 (2 h)	40
Pd/C	100 (7 h)	39
Pt/C	85	47
BiPt/C	90	43
SnPt/C	80	63
SnPd/C	40	61
SnRu/C	75	50

In conclusion, we can say that the hydrogenation of D-fructose to D-mannitol and D-glucitol can be conducted under very mild conditions (70 °C, 1 bar H_2) using Ru/C catalysts. Under these conditions, the furanose forms are hydrogenated preferentially, fructopyranose is less reactive. The adsorption constants of fructopyranose, fructofuranose and the hydrogenation products are of the same order of magnitude, which results in inhibition of the hydrogenation by fructopyranose, D-mannitol and D-glucitol.

Although the carbon surface chemistry does not directly influence the reaction rate, it influences the location of the Ru particles. A better wettability, either by using a less polar impregnation solvent or by using a more hydrophilic carbon, results in a Ru surface better accessible to D-fructose. The particle size, however, is not strongly influenced by the wettability. The Ru particles of the different catalysts were below or just above the detection limit (0.5 nm) of the TEM microscope.

Tin appeared to be a good promoter for high D-mannitol selectivities. SnPt/C and SnPd/C increased the D-mannitol selectivity from 42 to 62%. This promising result deserves further study.

3. Experimental

Materials.—Two carbons were used: a steam activated peat-based carbon (SX1G) and a chemically activated wood-based carbon (Darco-KBB), both donated by Norit. SX1G (10 g) was refluxed in 150 mL of 65% HNO_3

for 1 h. After washing and drying at 80 °C, the carbon denoted as SX1GN65 was obtained.

A 5 wt% Ru/C, a 5 wt% Pt/C catalyst and methyl α-D-glucopyranoside were purchased from Acros Chimica N.V. (Geel, Belgium), D-fructose (anhydrous) and D-glucose (anhydrous) were obtained from E. Merck KGaA (Darmstadt, Germany) and isomaltulose was a gift from Südzucker. $RuCl_3 \cdot x\ H_2O$ (40 wt% Ru) was a gift from Johnson Matthey (Hertfordshire, UK). Other Ru/C catalysts were home-made (see below). A 2.5 wt% Pd/C catalyst was a gift from Engelhard De Meern BV (De Meern, The Netherlands). This catalyst was based on Norit SX1G.

Catalyst preparation.—The Ru/C catalysts were prepared by incipient wetness impregnation of the carbon (0.95 g) with a solution of 110 mg $RuCl_3 \cdot 2.5\ H_2O$ in 2.0 mL solvent. Three solvents were used: water, EtOH and acetone. After drying overnight at ambient conditions and 3 h at 80 °C, the catalysts were reduced in a 10% H_2/N_2 flow for 2 h at 400 °C. Before reduction, water was removed at 120 °C (1 h) under a nitrogen flow. After reduction, the catalysts were cooled down to room temperature (rt) under N_2 atmosphere and then the oxygen concentration was slowly (1% per 5 min) raised to 20% O_2/N_2.

Catalyst promotion.—Tin-promoted catalysts were prepared by deposition of 1% Sn on 5 wt% Ru/C, and on commercial 2.5% Pd/C and 5% Pt/C catalysts by the following procedure. Under a N_2 atmosphere, 30 mL of an aq soln of $SnCl_4 \cdot 5\ H_2O$ (138 mg) was slowly (0.8 mL min^{-1}) added to the catalyst suspension (3.8 g/50 mL water), pre-reduced under H_2. The pH of the suspension was increased to 8.5 using 1 M NaOH. The suspension obtained was filtered off, the catalyst was washed until neutral and dried in air, first one night at rt and then 3 h at 120 °C. A Bi-promoted Pt/C catalyst was prepared similarly using $BiONO_3$ [22].

Catalyst characterization.—The amount of acid sites on the carbon surface was determined by selective neutralization with NaOH, according to the method of Boehm [23]. To 100 mg of carbon, 10 mL of 0.05 M NaOH was added. After shaking the suspension for 4 days, the carbon was centrifuged, washed and filtered over a 0.45 μm filter (Chromofil), and titrated with 0.05 M HCl.

An indication of the amount of carboxylic acid sites was obtained by infrared spectroscopy. Infrared spectra were recorded with a Perkin–Elmer spectrum 1000 FTIR spectrometer. KBr tablets were used containing 2 mg of carbon in 250 mg KBr. The spectra were obtained by co-adding 20 spectra with a resolution of 4 cm^{-1}. The original spectra were corrected for a curved baseline.

The metal loadings on the support were measured by Mr J. Padmos, using X-ray fluorescence spectroscopy, XRF (Philips PW1480). The Ru particles were studied with TEM using a Philips CM 30 T electron microscope, combined with energy dispersive analysis of X-rays (EDX). CO adsorption measurements were performed by the pulse method at rt, after reduction in 15% H_2/Ar at 100 °C.

Hydrogenation experiments.—The hydrogenation experiments at elevated pressure were performed in a Parr 4842 autoclave made of Hastelloy C276. A 50 mL aq suspension of the catalyst was introduced into the autoclave. The system was flushed with nitrogen and hydrogen and heated to the desired temperature under 10 bar H_2. After that, a 30 mL solution of D-fructose in water was introduced in the system and the H_2 pressure was adjusted to the desired value.

The reactions at 1 bar H_2 pressure were performed in a glass batch reactor of 200 mL, equipped with a gas-tight stirrer and a thermostatic bath. Prior to each experiment, the system, including a 50 mL aq suspension of the catalyst, was flushed with N_2. After that, the system was heated to the desired temperature and the catalyst was pre-reduced by flushing the system with H_2 for 30 min. The reaction was started by adding D-fructose.

Unless stated otherwise, the following conditions were applied: 72 °C, 1 bar H_2, 1500 rpm, 0.07 M D-fructose (1 g in 80 mL of water) and 0.05 g of Ru/C catalyst.

Samples taken during the reaction were analyzed by high-performance liquid chromatography (HPLC) using a Millipore-Waters 590 pump and a 300×7.8 mm cation exchange

column in the Ca^{2+} form (Phenomenex), connected to a refractive index detector (Shodex RI SE-51). The samples were eluted with degassed water at a flow rate of 0.6 mL min^{-1} and a column temperature of 80 °C.

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References

[1] For a review on D-mannitol synthesis, see: M. Makkee, A.P.G. Kieboom, H. van Bekkum, *Starch*, 37 (1985) 136–141.
[2] Chemical Market Reporter, September 13 (1999) 46–53.
[3] M. Makkee, A.P.G. Kieboom, H. van Bekkum, J.A. Roels, *J. Chem. Soc., Chem. Commun.*, (1980) 930–931.
[4] M. Makkee, A.P.G. Kieboom, H. van Bekkum, *Starch*, 37 (1985) 232–241.
[5] P. Gallezot, M. Besson, *Carbohydr. Eur.*, 13 (1995) 5–10.
[6] F. Joó, Z. Tóth, M.T. Beck, *Inorg. Chim. Acta*, 25 (1977) L61–L62.
[7] S. Kolaric, V. Šunjic, *J. Mol. Catal. A*, 110 (1996) 189–193.
[8] M. Makkee, A.P.G. Kieboom, H. van Bekkum, *Carbohydr. Res.*, 138 (1985) 225–236.
[9] A.W. Heinen, J.A. Peters, H. van Bekkum, *Appl. Catal.*, 194–195 (2000) 193–202.
[10] J.A. Dean, *Lange's Handbook of Chemistry*, McGraw-Hill, New York, 1992, pp. 4–16.
[11] L.W. Wright, *Chemtech*, (1974) 42–46.
[12] F. Kapteijn, J.A. Moulijn, R.A. van Santen, in J.A. Moulijn, P.W.N.M. van Leeuwen, R.A. van Santen (Eds.), *Catalysis. An integrated Approach to Homogeneous, Heterogeneous and Industrial Catalysis*, Elsevier, Amsterdam, 1993, pp. 69–86.
[13] P.G.J. Koopman, Ph.D. Thesis, Delft University of Technology, The Netherlands, 1980.
[14] S.J. Angyal, *Adv. Carbohydr. Chem. Biochem.*, 42 (1984) 15–68.
[15] A.E. Flood, M.R. Johns, E.T. White, *Carbohydr. Res.*, 288 (1996) 45–56.
[16] J.F. Ruddlesden, A. Steward, D.J. Thompson, R. Whelan, *Faraday Discuss. Chem. Soc.*, 72 (1981) 397–411.
[17] V. Machek, J. Hanika, K. Sporka, V. Ruzicha, J. Kunz, L. Janacek, in G. Poncelet, P. Grange, P.A. Jacobs (Eds.), *Preparation of Catalysts III*, Elsevier, Amsterdam, 1983, pp. 69–80.
[18] S. Galvagno, A. Donato, G. Neri, R. Pietropaolo, G. Capannelli, *J. Mol. Catal.*, 78 (1993) 227–236.
[19] L. Stievano, S. Calogero, F.E. Wagner, S. Galvagno, C. Milone, *J. Phys. Chem. B*, 44 (1999) 9545–9556.
[20] Y. Pouilloux, F. Autin, C. Guimon, J. Barrault, *J. Catal.*, 176 (1998) 215–224.
[21] V.M. Despehande, K. Ramnarayan, C.S. Narasimhan, *J. Catal.*, 121 (1990) 174–182.
[22] A.W. Heinen, J.A. Peters, H. van Bekkum, *Carbohydr. Res.*, 304 (1997) 155–164.
[23] H.P. Boehm, *Adv. Catal.*, 16 (1966) 179–274.