Factors effecting the hydrogenation of fructose with a water soluble Ru–TPPTS complex. A comparison between homogeneous and heterogeneous catalysis

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Abstract

Inulin, a polysaccharide containing one D-glucose and 10 to 50 D-fructose units, when hydrolysed and hydrogenated in a one pot approach, would be an attractive D-mannitol feedstock. For this purpose, the hydrogenation was studied with fructose as a model compound, using a water soluble, homogeneous catalyst. This catalyst contains ruthenium as the active metal, and trisulfonated triphenylphosphine (TPPTS, $P(m\text{-}C_6H_4SO_3Na)_3$), as the ligand. The effects of temperature, pressure, catalyst/substrate and ligand/metal ratios on the activity and selectivity were investigated. The reaction was shown to be homogeneously catalysed, despite the formation of some ruthenium particles at higher temperatures ($> 90°C$), and the active complex was studied with ^1H and ^{31}P NMR. Addition of HCl or salts (NaCl, NaI and $CaCl_2$) increased the selectivity to D-glucitol and the catalytic activity. Upon deuterogenation of fructose with H_2 in D_2O, D was built in only at the 2-position. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The sweetener D-mannitol can be obtained from the relatively expensive sources D-fructose and D-mannose, in yields of about 45 and 100%, respectively. For economical reasons, D-mannitol is prepared by hydrogenation of a 1:1 mixture of D-glucose and D-fructose, obtained from sucrose, usually with Raney nickel or noble metals as catalysts. 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 the inexpensive D-glucose with 100% selectivity. This explains why D-mannitol is the more expensive product. Inulin, a polysaccharide containing one D-glucose and 10 to 50 D-fructose units, would seem a more attractive D-mannitol feedstock (see Scheme 1).

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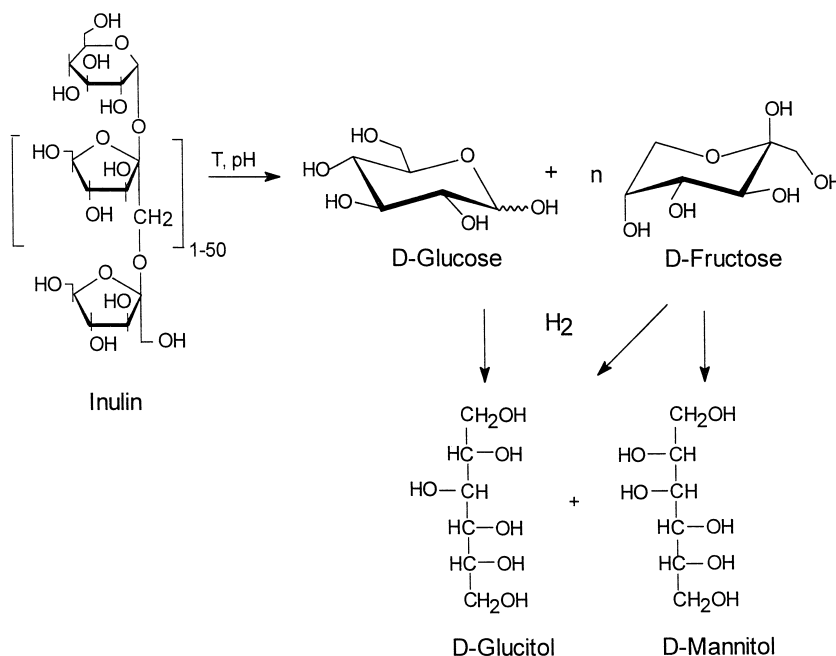
Scheme 1. Hydrolysis and hydrogenation of inulin.

In the hydrogenation of D-fructose on various heterogeneous catalysts, the selectivity to D-mannitol is about 45%. Only copper has been reported to give a higher selectivity (67%) [1]. To obtain D-mannitol from inulin, hydrolysis to the monosaccharides is necessary. Therefore, a catalyst combining an acidic with a hydrogenating function would be ideal. An option is the use of acidic zeolites as catalyst support [2]. So far, however, the performance of heterogeneous catalysts in reactions of inulin has been poor [3,4].

This paper describes the hydrogenation of D-fructose and inulin, catalysed by a water soluble homogeneous Ru–TPPTS (TPPTS = P(m-C$_6$H$_4$SO$_3$Na)$_3$) catalyst. Previously, homogeneously catalysed hydrogenations of D-fructose, using RuCl$_2$(PPh$_3$)$_3$ and RuHCl(PPh$_3$)$_3$ in dimethylacetamide as the solvent, have been described [5,6]. Homogeneously catalysed hydrogenation of D-fructose in water was reported by Joó et al. [7], who applied Ru(II) as the active metal and monosulfonated triphenylphosphine (TPPMS) as the ligand. Kolaric and Šun-

jic [8] hydrogenated D-glucose and D-mannose with the trisulfonated ligand TPPTS, which has a higher solubility.

2. Experimental

2.1. Materials

D-Fructose (extra pure), CaCl$_2 \cdot$ 2H$_2$O and a phosphate buffer pH 7 (Titrisol) were obtained from Merck (Darmstadt, Germany). Inulin, with a degree of polymerisation of 10, was a gift from Sensus (Coöperatie Cosun, Roosendaal, The Netherlands). NaI $\cdot$ 2H$_2$O and a 5 wt.% Ru/C catalyst were purchased from Acros Chimica (Geel, Belgium) and NaCl and D-glucose (anhydrous) from J.T. Baker Chemicals (Deventer, The Netherlands). The activated carbon, Norit Darco KBB, was a chemically activated wood-based carbon and was donated by Norit (Amersfoort, The Netherlands). RuCl$_3 \cdot$ xH$_2$O (40 wt.% Ru) was a gift from Johnson Matthey (Hertfordshire, UK), TPPTS, sodium

form, was prepared according to the procedure of Hoechst [9] and D_2O was obtained from the Cambridge Isotope Laboratories (Andover, USA).

2.2. Reaction procedure and analysis

Under argon atmosphere, 21 mg $RuCl_3 \cdot 2.5H_2O$ (0.083 mmol) and 249 mg TPPTS (0.4 mmol) were added to 50 ml of deoxygenated, distilled and demineralised water. After stirring for 40 min, a dark green solution of pH 2.3 was obtained. The substrate, i.e. D-fructose or inulin (5.4 g), was degassed and, together with the catalyst solution, introduced into a Parr 4842 autoclave, made of Hastelloy C276; all under Ar atmosphere. In order to work under constant H_2 pressure, the reaction mixture was heated up under N_2. As soon as the desired temperature was reached, the H_2 pressure was applied. Samples, taken during the experiment, showed the formation of a yellow solution, already during heating-up.

Samples taken were analysed by 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.

The hydrogenation of D-fructose was optimised by varying the temperature and the H_2 pressure. Unless stated otherwise, the following conditions were applied: 90°C, 100 bar H_2, pH 2.3, TPPTS/Ru = 4.8, D-fructose/Ru = 375 and D-fructose 0.60 M.

Deuterogenation experiments were performed both with H_2 and D_2 and with, respectively, D_2O and H_2O as the solvent.

2.3. Analysis of particles

The nature of any solid particles formed during the reaction was determined with X-ray fluorescence spectroscopy, XRF (Philips PW1480). The size of the particles was measured by photon correlation spectroscopy (PCS). The PCS measurements were conducted at an angle of 90°, using an argon laser with a wavelength of 514.5 nm and a BI-200SM goniometer, coupled to a BI-8000AT autocorrelator. The data were analysed using the CONTIN method [10]. Dust-free water was used as reaction medium.

2.4. NMR experiments

The Ru–TPPTS complex was studied on samples taken during the reaction with ^1H NMR and ^{31}P NMR, using a Varian Unity-Inova 300 spectrometer. One percent H_3PO_4 in D_2O was used as the external reference (substitution method). The reaction mixture contained 10% D_2O. All sample handling of reaction mixtures was under Ar. ^{13}C NMR on D-fructose–$RuCl_3$ solutions was measured with D_2O as solvent and *t*-BuOH as internal reference (CH$_3$, δ 31.2 ppm).

3. Results and discussion

The Ru–TPPTS catalysts used in this study were prepared by direct addition of $RuCl_3$ to TPPTS in aqueous solutions. This is easier than an ex situ preparation of the catalyst. Moreover, Hernandez and Kalck [11] obtained good results in the hydrogenation of aldehydes with in situ preparation of this complex. First, we investigated the performance of this catalytic system in the hydrogenation of D-fructose. Subsequently, we studied the combined hydrolysis and hydrogenation of inulin.

3.1. Effect of temperature and pressure

Fig. 1a and b present the activity of the catalyst in the hydrogenation of D-fructose as a function of temperature and hydrogen pressure,
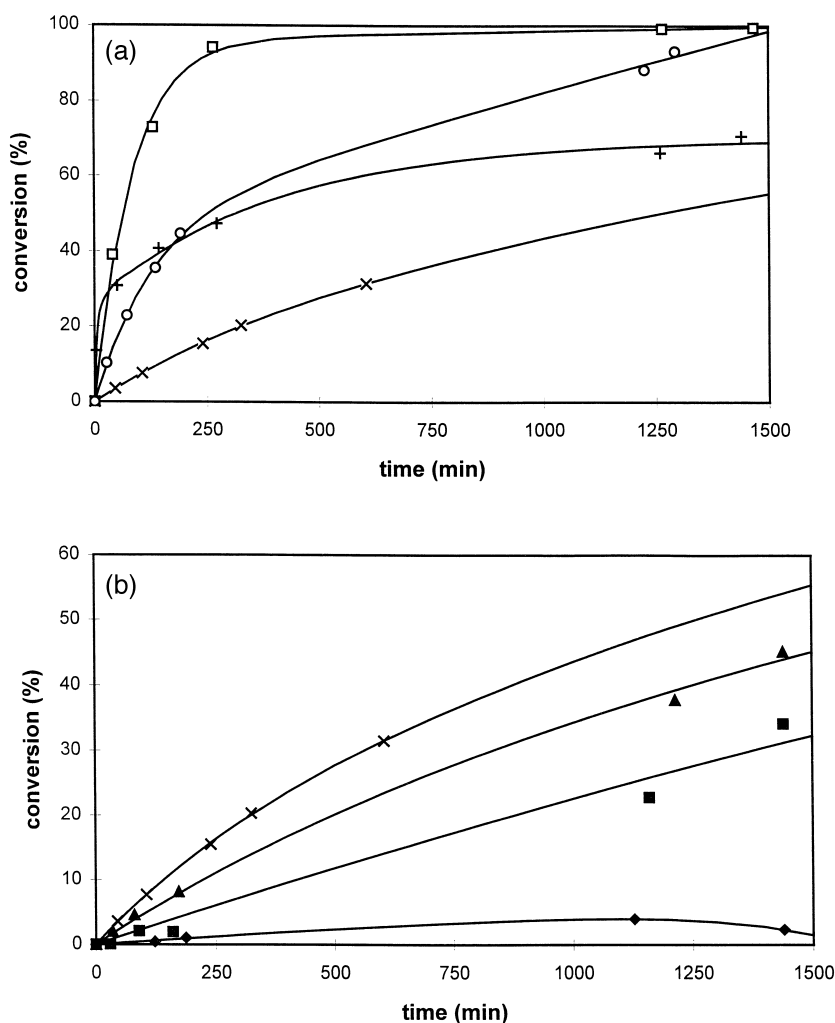
Fig. 1. (a) Hydrogenation of fructose at 100 bar H_2 and different temperatures: $\times$ 70°C; $\bigcirc$ 90°C; $\square$ 100°C; + 125°C; and (b) at 70°C and different pressures: $\blacklozenge$ 1 bar; $\blacksquare$ 25 bar; $\blacktriangle$ 50 bar; $\times$ 100 bar. TPPTS/Ru = 4.8; pH 2.3; fructose/Ru = 375; 0.60 M fructose in 50 ml H_2O. The curves are a guide to the eye.

respectively. The activity increases with pressure and with temperature up to 100°C. However, at 125°C the catalyst deactivates after a few minutes. All samples taken at this temperature contained black particles, just like samples of the reaction at 100°C after prolonged reaction times ($t > 1000$ min). X-ray fluorescence spectroscopy (XRF) identified the black particles as Ru(0). Therefore, we conclude that the catalyst is not stable in the presence of hydrogen at temperatures above 90°C. Instability of Ru–

TPPTS complexes above 150°C in the presence of hydrogen was previously reported by Fache et al. [12].

When ln[D-fructose] is plotted against time for different temperatures and starting concentrations of D-fructose, straight lines were obtained showing the reaction to be first order in D-fructose. The rate constants at different temperatures are presented in Table 1. The apparent activation energy, calculated with these data, amounts to 93.6 kJ/mol.

Table 1
Effect of temperature on the initial reaction rate; 100 bar H_2; pH 2.3; TPPTS/Ru = 4.8; [fructose]/Ru = 375; 0.60 M D-fructose in water (50 ml)

Temperature (°C)	k (h^{-1})
70	0.04
90	0.26
100	0.64

3.2. Homogeneous or heterogeneous catalysis

In Fig. 2a the effect of the ligand/metal ratio on the activity is presented. Catalysts with TPPTS/Ru ratios of 4.8 and 12 showed exactly the same performance. Zero order kinetics in

TPPTS was earlier reported by Fache et al. [12] for the hydrogenation of propionaldehyde. However, in the absence of TPPTS a much higher activity was observed and a suspension of black particles was obtained, which were identified to be Ru(0) metal by XRF. ^{13}C NMR measurements on a solution of D-fructose and RuCl$_3$ (1:1), both after standing at 25°C and after one night at 90°C, did not give any evidence for complexation of D-fructose to Ru^{3+}. Therefore, we can conclude that the reaction in the absence of TPPTS is heterogeneously catalysed.

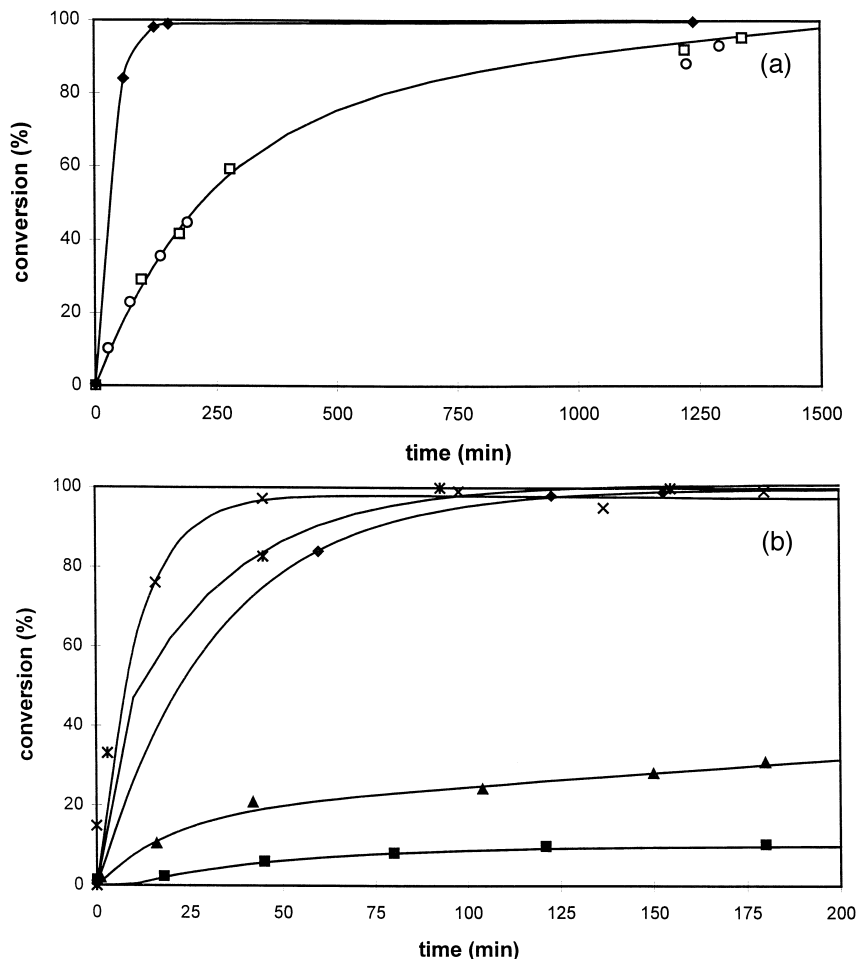Further support for the heterogeneous character of this reaction was obtained from the fol-

Fig. 2. (a) Hydrogenation of fructose with different TPPTS/Ru ratios: ♦ 0; ○ 4.8; □ 12; (b): Hydrogenation with Ru, after prereduction of RuCl$_3$. ♦ no prereduction, ■ 1 h, ▲ 8 min, × 8 min + carbon added (192 mg), ∗ 5 wt.% Ru/C; conditions: 90°C, pH 2.3, 100 bar H_2, fructose/Ru = 375; 0.60 M fructose in 50 ml H_2O. The curves are a guide to the eye.

lowing series of experiments. $RuCl_3$ was pre-re-duced for either 1 h or 8 min (10 bar H_2, 90°C), both with and without the presence of activated carbon (Norit Darco KBB). After that, D-fructose was added. It is expected that with longer pre-reduction times larger metal particles and consequently a smaller active surface area will be obtained. In the presence of a support like activated carbon, a higher and more stable metal dispersion is expected. Indeed, a substantially higher activity was observed (see Fig. 2b).

A commercial 5 wt.% Ru/C catalyst is more active (on a Ru weight base) than the Ru–TPPTS complex in the hydrogenation of D-fructose. Addition of TPPTS to the Ru/C (molar ratio TPPTS to Ru 1.2), however, decreased the D-fructose conversion from 98% in 90 min to 86% in 180 min. Probably, TPPTS adsorbs onto the metal surface and acts as an inhibitor.

The results of the experiments described above give rise to the question whether the hydrogenation of D-fructose is actually homoge-neously catalysed by a Ru–TPPTS complex. To verify whether small, colloidal particles were formed, analogous to the observations of Lar-pent and Patin [13] in the hydrogenation of olefins with RhTPPTS, photo correlation spec-troscopy (PCS) experiments were conducted. These experiments showed that no colloidal par-ticles were formed (upper detection limit 1 μm).

Moreover, a recycle experiment was per-formed. After 3 h hydrogenation (at 90°C), the reaction mixture was divided in three portions. These portions were re-used again (with addi-tional water and D-fructose) after filtration over a 0.2 μm filter (Whatman) and over a 0.45 μm filter (Chromofil), and without filtration. In all three experiments the conversion of D-fructose after 3 h was exactly the same, i.e. 20%, al-though this is half of the activity in the first reaction cycle (40% in 3 h). This decreased activity upon re-use is probably due to partial oxidation of the catalytic complex.

It can be concluded that this reaction is ho-mogeneously catalysed, although some metallic Ru particles are formed at temperatures exceed-ing 90°C. Probably, these particles formed at higher temperature are too large to contribute significantly to the overall catalytic activity. Moreover, the heterogeneously catalysed reac-tion is inhibited by adsorption of TPPTS. The zero order observed in TPPTS (Fig. 2a) under-lines the homogeneous character of the 90°C experiment.

3.3. Structure of the catalyst

The Ru–TPPTS complexes were studied with ^{31}P NMR. A $RuCl_3$/TPPTS (1:4.8) mixture, immediately after preparation, displayed ^{31}P resonances for free TPPTS (δ −5.7 ppm, 87%), TPPTS oxide (OTPPTS, δ 34.5 ppm, 8%), $[Ru(Cl)(\mu Cl)(TPPTS)_2]_2$ (δ 57.1 ppm, 3%, Ref. [14]), and a small amount of an unidentified compound (δ 5.6 ppm, 2%). The percentages refer to the percentage of the summed signal intensities in the ^{31}P NMR spectra. After heat-ing at 90°C for 1 h, two extra peaks appeared (35.6, 2% and 56.8 ppm, 7%). The intensity of the ^{31}P NMR signal for free ligand decreased to 53%, whereas the intensities of the signals of OTPPTS and of the complex increased to 16% and 8%, respectively. This oxidation of TPPTS can be explained by a simultaneous reduction of Ru^{3+} to Ru^{2+} [15].

In a second experiment D-fructose was added and the molar ratio was adjusted to the reaction formulation. After heating the reaction mixture in the autoclave (1 h, 90°C), additional peaks at 56.7 (2%) and about 58 ppm (broad, 18%) were observed, which were assigned to the binuclear complexes $[Ru_2(Cl)_2(\mu Cl)_2(TPPTS)_4]$ and $[Ru_2(H_2O)_2(\mu Cl)_2(TPPTS)_4]Cl_2$, respectively [14]. A peak at 23.2 ppm indicated the forma-tion of a phosphonium salt [14]. ^{1}H NMR did not show any evidence for coordination of D-fructose directly to the metal. After 3 h of reaction (100 bar H_2), ^{31}P NMR revealed new signals at 79.0 an 82.3 ppm, besides those of TPPTS, OTPPTS and phosphonium salts. In the ^{1}H NMR spectrum, no hydride signals were observed. Hernandez and Kalck [11] observed a

singlet at 82.4 ppm in the hydrogenation of *trans*-4-hexen-3-one, which was assigned to $[Ru(H)(Cl)(TPPTS)_2(H_2O)]$. Probably, the signal at 79.0 ppm is due to $[Ru(H)(Cl)_2(TPPTS)_2]$. After one night, the signals at 79.0 and 82.3 had disappeared, but signals at 73.6 and 44.9, and a very broad peak around 57 ppm, appeared. These signals could be due to a D-fructose containing complex.

In the absence of D-fructose, a solution was obtained, showing ^{31}P resonances for free TPPTS (34%), OTPPTS (23%) and for a Ru-complex (43%). The complex showed signals at 57.1 and 56.8 ppm (5%) on a very broad peak around 57 ppm (38%), which indicates the presence of the dimeric species described above. In conclusion, the catalytic active species are most probably the hydride species, originating from $[Ru(Cl)(\mu Cl)(TPPTS)_2]_2$.

A deuterogenation experiment of fructose with D_2 in water showed that almost no D was built in into fructose, but a substantial amount of D (7%) was found in the water. Apparently, the deuteride complexes $Ru(D)(Cl)(TPPTS)_2$ (H_2O) and $Ru(D)(Cl)_2(TPPTS)_2$ react more readily with water, under the formation of HD and/or HDO, than with fructose. This may also explain why hydride resonances of these species could not be observed in the ^1H NMR spectrum: probably the fast exchange between the hydride and H_2/H_2O causes extensive line broadening. The fast exchange enabled us to perform deuterogenation with the convenient system H_2/D_2O. ^{13}C NMR showed that upon hydrogenation of fructose in D_2O, D was built in at

Table 2
Effect of pH on the conversion of fructose and the selectivity to mannitol after 3 h; 90°C, 100 bar H_2; TPPTS/Ru = 4.8; [fructose]/[Ru] = 240; 0.38 M D-fructose in 50 ml water

pH	Conversion (%)	[D-Mannitol]/ [polyols]·100%
0.95	99	20
2.3	56	45
3.7	50	44
7	22	48

Table 3
Effect of salts on the conversion of fructose and the selectivity to mannitol after 3 h; 90°C, 100 bar H_2; TPPTS/Ru = 4.8; [fructose]/[Ru] = 240; 0.38 M D-fructose in 50 ml water; pH 2.3 (except upon addition of HCl)

Additive	Anion/ Ru	Cation/ Ru	Conversion (%)	Selectivity (%)
–	(3)	(14)	56	45
HCl	65	65	100	20
NaCl	68	68	100	24
NaI	74	74	100	24
$CaCl_2$	65	33	77	28
$CaCl_2$	130	65	94	23

C-2, which indicates that the reaction does not proceed via an enediol species, but either via hydrogenation of the open form or hydrogenolysis of the cyclic forms.

3.4. Mannitol / glucitol ratio

At all temperatures, pressures and metal/ligand ratios the selectivity to D-mannitol amounted to 41–46%. The same D-mannitol/D-glucitol ratio was obtained in the experiments starting with only $RuCl_3$ and with Ru/C. However, upon decrease of the pH of the homogeneously catalysed reaction mixture to 0.95, by addition of HCl to the starting solution, the selectivity changed substantially (Table 2), and
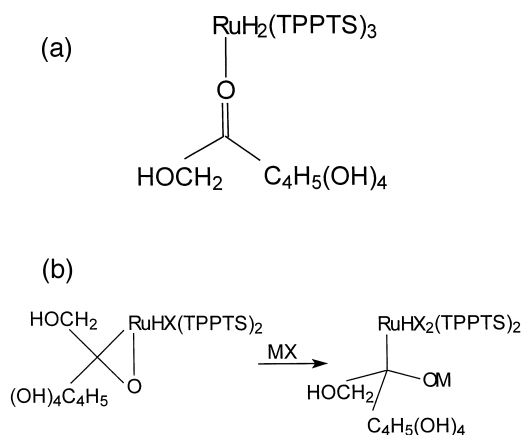

Fig. 3. Coordination of fructose to the catalyst in the absence (a) and presence (b) of salt (MX) M denotes the metal, × the cation [12].

the activity increased significantly. Upon increasing the pH, by adding NaOH or by working in a phosphate buffer at pH 7, no change in the D-mannitol/D-glucitol ratio was observed. This suggests that the change in selectivity can be ascribed to an anion and/or cation effect. In a reaction catalysed by Ru/C, no pH effect was observed.

At pH 7 D-fructose to D-glucose isomerisation was observed. A blank reaction in the phosphate buffer also showed conversion of D-fructose to D-glucose. This effect of sodium phosphate solutions on the isomerisation was

already reported in 1929 by Spoehr and Strain [16].

The effect of both anions and cations was confirmed by similar effects observed upon addition of different salts (Table 3). The promoting effect of salts on the activity of Ru–TPPTS complexes in the hydrogenation of propionaldehyde was reported earlier by Fache et al. [12]. The anion effect was explained by the formation of a different catalytic species: $RuHX(TPPTS)_3$, where X denotes the anion. The influence of the cation was explained in the following way. In the mechanism without salt, the oxygen atom of
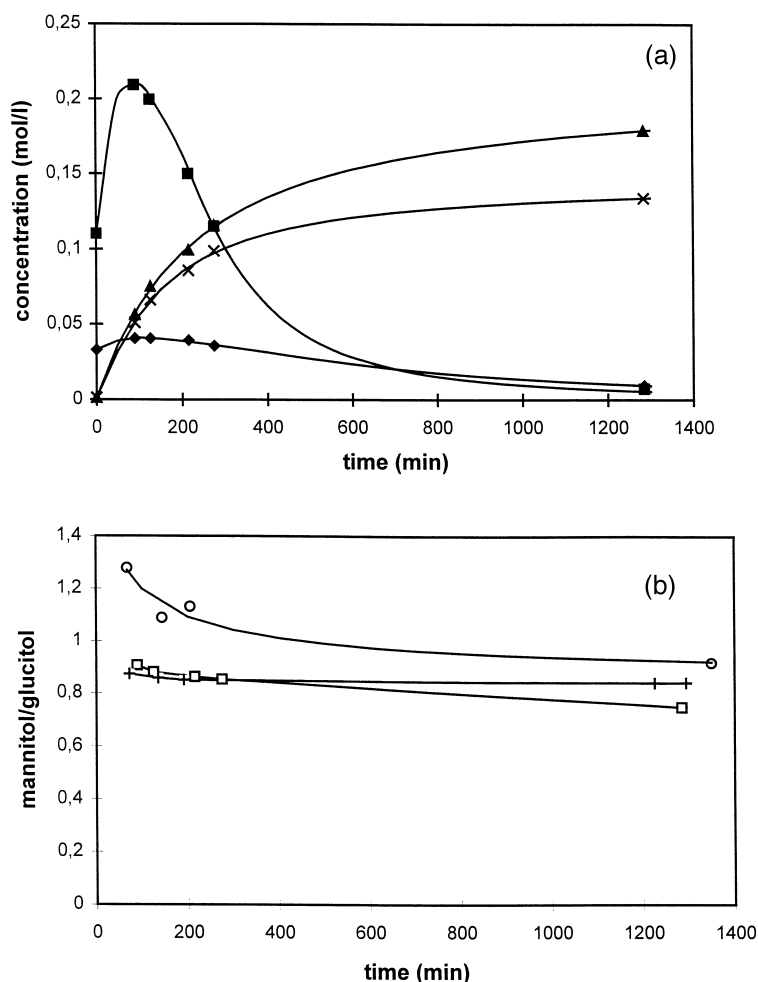

Fig. 4. Combined hydrolysis and hydrogenation of inulin using RuTPPTS. (a) Concentration of glucose (♦), fructose (■), mannitol (X) and glucitol (▲) (pH 2.3); (b): mannitol/glucitol ratio vs. time for the hydrogenation of fructose at pH 2.3 (+), inulin at pH 2.3 (□) and inulin at pH 3.3 (○); conditions: 90°C, 100 bar H_2, TPPTS/Ru = 4.8, [monosaccharide units] = 0.40 mol/l. The curves are a guide to the eye.

the ketone coordinates to the metal (Fig. 3a), whereas in the presence of salt, the coordination of the carbon atom to the catalyst is favoured by the cation (Fig. 3b).

This difference in coordination might also explain the selectivity change in the presence of salts. In this mechanism, the ruthenium coordinates to the carbon atom of the ketone group. Hence, steric effects favouring the formation of one isomer, are expected to be more important than when Ru is coordinated to oxygen.

3.5. Hydrolysis and hydrogenation of inulin

Fig. 4a presents the formation of D-mannitol and D-glucitol during the combined hydrolysis and hydrogenation of inulin (dp 10) with Ru–TPPTS at pH 2.3. It shows that inulin, due to the acidic environment the catalyst creates, can be hydrolysed to D-glucose and D-fructose. As stated before, D-fructose is hydrogenated to D-mannitol and D-glucitol, whereas D-glucose affords exclusively D-glucitol. The presence of D-glucose and D-fructose during the reaction shows that the hydrogenation is the rate limiting step.

In Fig. 4b the D-mannitol/D-glucitol ratio for the hydrogenation of D-fructose and inulin as a function of time and pH is given. The molar ratio D-mannitol/D-glucitol decreases somewhat in time, especially in the case of inulin. An experiment with D-glucose as the substrate (90°C, 100 bar H_2, D-glucose/Ru = 375) pointed out that the initial rate of the hydrogenation of D-glucose is 2.5 times lower than that of D-fructose. In a competition experiment, in which both glucose and fructose were present, glucose inhibited the hydrogenation of fructose. Therefore, we can conclude that glucose coordinates stronger to the Ru complex than fructose. The nature of this coordination is an object of further investigation.

When most of the D-fructose was hydrogenated in the inulin experiment, the hydrogenation of D-glucose and therefore, the formation of D-glucitol, becomes more pronounced and the

D-mannitol/D-glucitol ratio decreases somewhat (Fig. 4b).

However, this does not explain the relatively high D-mannitol/D-glucitol ratio obtained in the hydrogenation of inulin at pH 3.3. At this pH, the hydrolysis is relatively slow with respect to the hydrogenation. Perhaps, the stereoselectivity of the hydrogenation of D-fructose units in partially hydrolysed oligomers is higher than that of the hydrogenation of D-fructose itself. It may be noted that inulin upon hydrolysis gives the non reducible GF_x and F_y. The latter species possesses a reducible group.

4. Conclusion

Homogeneous catalysis, using Ru as the active metal ion and the water soluble TPPTS as the ligand, is suitable for the combined hydrolysis and hydrogenation of inulin. The use of this D-fructose polymer as a feedstock for the production of various products is promising. The advantage of homogeneous catalysis is the perspective of directing the selectivity. In this system the selectivity to D-glucitol can be increased by addition of HCl or salts like $CaCl_2$, NaCl and NaI. In the hydrogenation of inulin the selectivity to D-mannitol is higher than expected, particularly at higher pH (≥ 3.3).

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