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Catalysis Today 52 (1999) 349–361

CATALYSIS TODAY

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Catalytic hydrogenation of fine chemicals: sorbitol production

K. van Gorp[a,*], E. Boerman[a], C.V. Cavenaghi[b], P.H. Berben[a]

[a]Engelhard De Meern B.V., PO Box 19, 3454 ZG De Meern, The Netherlands
[b]Engelhard Italiana S.p.A., Via Ronchi, 17, 20134 Milan, Italy

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Abstract

Historically, skeletal nickel is the catalyst of choice in the production of sorbitol on industrial scale. A disadvantage of the use of skeletal nickel in the hydrogenation of glucose containing feedstocks to sorbitol, is the fact that a part of the nickel leaches. As a consequence, purification of the sorbitol is required, which renders this process economically less attractive. To meet the demand for non-leaching catalyst systems, ruthenium on carbon catalyst are presently becoming more important. In this paper, a comparison is made between different 5% Ru on carbon catalysts in the hydrogenation of a dextrose monohydrate and a very high maltose feedstock. The influence of the carbon support, the ruthenium metal location, and the applied ruthenium precursor are investigated. For comparison reasons, both skeletal Ni and Ru catalysts have been applied in the hydrogenation of dextrose to sorbitol. The effect of reaction temperature and pressure during the hydrogenation of a very high maltose containing feedstock is also investigated. It is shown that Ru catalysts are suitable alternatives for skeletal Ni catalysts in respect to re-usability, activity and selectivity.

Keywords: Catalytic hydrogenation; Fine chemicals; Sorbitol; Ruthenium; Nickel

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1. Introduction

Hydrogenation of carbohydrates is a major process in fine chemical (food) industry [1,2]. Historically, glucose is hydrogenated to sorbitol over (skeletal) Ni catalysts [1–4]. For decades, sorbitol has been applied as sweetener in ‘‘sugar free’’ food products intended for diabetics [5,6]. Even today, despite the major contribution of synthetic sweeteners such as aspartame, sorbitol is still frequently applied as sweetener in all kinds of food products. Furthermore, sorbitol is applied as starting material for vitamin C synthesis [5–9].

One of the advantages of the use of a skeletal Ni catalyst in the hydrogenation of glucose to sorbitol is its relative low price compared to other more expensive catalyst systems. However, during the hydrogenation of glucose to sorbitol dissolution of nickel will occur [1,2] (as a consequence, purification of the sorbitol is necessary and renders this process economically less attractive). Therefore, alternative heterogeneous catalysts have been tested, including the supported metals such as cobalt, platinum, palladium, rhodium, and ruthenium [3,4,10]. The most promising catalysts are the supported ruthenium catalysts. The general observed order of activity for the hydrogenation of glucose is as follows [3,4]: Ru>Ni>Rh>Pd. Ruthenium does not dissolve under the conditions required for the hydrogenation of glucose to sorbitol.

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*Corresponding author. Tel.: +31-30-6669381; fax: +31-30-6669369
E-mail address: klaas.vangorp@engelhard.com (K. van Gorp)

PII: S0920-5861(99)00087-5

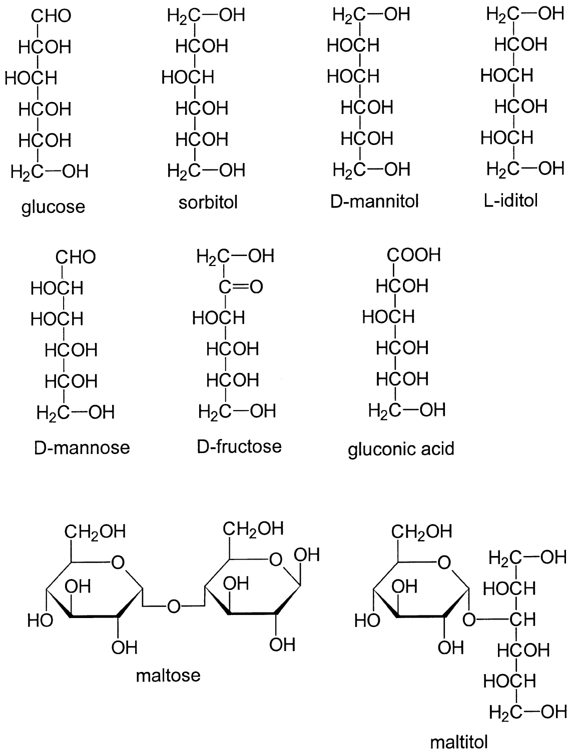

Fig. 1. Structures of the "sugars" mentioned in this paper.

Furthermore, availability and recycling of Ruthenium has improved significantly over the last years.

Generally, glucose is hydrogenated to sorbitol at 100–140°C, and hydrogen pressures ranging from 10 to 125 atm [8]. During this hydrogenation, several by-products can be formed. Especially in alkaline environments, glucose can isomerize to fructose and mannose [8]. Hydrogenation of fructose and mannose yields mannitol, as well as sorbitol. Furthermore, the high concentration of sorbitol at the end of the hydrogenation reaction induces isomerization of the sorbitol to iditol. In Fig. 1, structure of the "sugar" molecules mentioned in this paper are represented.

In this paper several items related to the application of Ru catalyst in the production of sorbitol are addressed. We have focused on the influence of the carbon support, the applied Ru metal precursor during the catalyst production, the Ru metal location, the reusability of Ru on carbon catalysts, the composition of the feed and the reaction temperature. Furthermore, a comparison is made with a commercially available skeletal nickel catalysts.

2. Experimental

2.1. *Materials*

The dextrose mono hydrate de-ionized water feedstock consisted out of a 50% dry solids containing 99.6% glucose and 0.4% maltose (on a dry solid base).

The very high maltose feedstock consisted out of a 50% dry solid solution obtained by dilution of a 67% dry solids solution, containing 4% glucose, 70% maltose and 18% maltotriose and 8% other oligosaccharides.

The hydrogen gas was applied as purchased from Hoekloos.

2.2. *Hydrogenation equipment*

All hydrogenations were performed in 316 stainless steel autoclaves (HP1 which is a 300 ml autoclave without baffles operated at 1600 rpm, and HP6 which is a 1000 ml autoclave equipped with two baffles operated at 1400 rpm) operated at the indicated H_2 pressure (40 or 60 bar). The autoclaves were equipped

Table 1
Physical properties of the 5% Ru on carbon catalysts

	Catalyst								
	MRP 9000	MRP 9017	MRP 40338	MRP 40339	MRP 40497	MRP 40498	MRP 40499	MRP 40420	MRP 40801
Support	CP86	CP97	CP97	CP97	CP87	CP97	CP97	CP97	CP97
Carbon type	Peat	Wood	Wood	Wood	Peat	Wood	Wood	Wood	Wood
SA	900	1100	1100	1100	950	1100	1100	1100	1100
PSD									
10%<	5	7	7	7	5	7	7	7	7
50%<	19	29	29	29	18	29	29	29	29
90%<	88	85	85	85	77	85	85	85	85
Metal distribution	Edge	Mixed	Uniform	Edge	Edge	Edge	Edge	Edge	Edge
Reducing agent	1	1	1	1	2	2	2	2	2
Ru precursor	a	a	a	a	b	b	b	b	b

SA=surface area of the carbon support in m^2/g, PSD=particle size distribution in μm. Since the manufacturing details of the Ru catalysts are considered to be confidential, process applied reducing agents and Ru precursors are indicated, respectively, with 1 or 2, and a or b. Note that catalysts 40498, 40499, 40420 and 40801 are produced with the same starting materials, but by different manufacturing techniques. Furthermore, catalyst 40801 is post treated to improve it's filterability.

with hollow shaft stirring rods. Temperatures ranged from 100°C to 140°C.

2.3. Catalysts

All applied 5% Ru catalysts are represented in Table 1. The skeletal Ni catalyst was purchased from a regular commercial source, such as Actimet C^{TM} (Engelhard), and applied as received.

2.4. Hydrogenation experiments

The catalyst loading was calculated on the basis of the dry solids present in the feedstock and represented as %. At the reported catalyst loadings no mass transport limitation occurred (determined up front in separate experiments performed at the same reaction conditions). In a typical hydrogenation experiment, the catalyst was suspended in 200 g feedstock at 50°C, and subsequently added into the autoclave. Hereafter, agitation was started, and the autoclave was three times flushed with nitrogen, and pressurized with hydrogen to 3 bar. The reaction mixture was heated to the desired reaction temperature, and the hydrogenation pressure was increased to the desired reaction pressure. The hydrogen uptake was monitored with a back pressure unit. When the hydrogen uptake ceased, the autoclave was flushed with nitrogen, and the catalyst was filtered off.

For re-use, the catalyst was washed with de-ionized water and re-suspended in fresh feed. Subsequently, the hydrogenation of the feed was performed as described above.

The hydrogenation conditions of the dextrose monohydrate experiments are represented in Table 2–4. In Tables 5 and 6 the hydrogenation conditions for the very high maltose feedstock are summarized.

2.5. Product analysis

Analysis of the reaction products was performed on a LDC analytical HPLC equipped with a Phenomenex Rezex Cal monosaccharide column (300 mm by 7.8 mm, 5 micron particles) operated at 85°C and a Refracto Monitor IV detector operated at 30°C. As eluens de-ionized water was applied, which was eluated at 0.6 ml/min.

The amount of reducing sugars was represented as % glucose and was determined according to literature methods described elsewhere [11].

3. Results and discussion

3.1. Dextrose monohydrate hydrogenation

The hydrogenation activities (performed at 100°C and 40 bar H_2) of all 5% Ru on carbon catalysts are shown in Fig. 2.

Table 2
Dextrose monohydrate hydrogenation parameters

	Catalyst							
	MRP 40420	MRP 40339	MRP 40338	MRP 40497	MRP 40498	MRP 40499	MRP 9000	MRP 9017
Catalyst load (%)	2	2	2	2	2	2	2	2
Autoclave	HP1	HP1	HP1	HP1	HP1	HP1	HP1	HP1
Feed (g)	200	200	200	200	200	200	200	200
Temperature (°C)	100	100	100	100	100	100	100	100
Pressure (bar)	40	40	40	40	40	40	40	40
Agitation (rpm)	1600	1600	1600	1600	1600	1600	1600	1600

Table 3
Dextrose monohydrate hydrogenation parameters used for re-use and comparison of MRP 9017, 40801 and skeletal Ni

	Catalyst								
	MRP 9017	MRP 9017	MRP 9017	MRP 40801	MRP 40801	MRP 40801	Sk Ni	Sk Ni	Sk Ni
Catalyst load (%)	1.5	1.5	1.5	0.75	0.75	0.75	4.5	4.5	4.5
Use	1st	2nd	3rd	1st	2nd	3rd	1st	2nd	3rd
Autoclave	HP6	HP6	HP6	HP6	HP6	HP6	HP6	HP6	HP6
Feed (g)	600	600	600	600	600	600	600	600	600
Temperature (°C)	120	120	120	120	120	120	120	120	120
Pressure (bar)	40	40	40	40	40	40	40	40	40
Agitation (rpm)	1400	1400	1400	1400	1400	1400	1400	1400	1400

Table 4
Dextrose monohydrate hydrogenation parameters for comparison of MRP 9017, 40801 at 100°C and 120°C

	Catalyst			
	MRP 40801	MRP 40801	MRP 9017	MRP 9017
Catalyst load (%)	0.75	1.25	1.5	2.5
Feed (g)	600	600	600	600
Temperature (°C)	120	100	120	100
Pressure (bar)	40	40	40	40
Agitation (rpm)	1400	1400	1400	1400

Table 5
Very high maltose feedstock hydrogenation parameters

	Catalyst					
	MRP 9017	MRP 40420	MRP 40497	MRP 9000	MRP 40339	MRP 40499
Catalyst load (%)	2	2	2	2	2	2
Autoclave	HP1	HP1	HP1	HP1	HP1	HP1
Feed (g)	200	200	200	200	200	200
Temperature (°C)	100	100	100	100	100	100
Pressure (bar)	40	40	40	40	40	40
Agitation (rpm)	1600	1600	1600	1600	1600	1600

From this plot, a general trend could be observed. All ruthenium catalysts prepared from precursor ‘‘b’’ were found to be more active than those prepared from precursor ‘‘a’’. However, one exception could be observed, the peat carbon supported catalyst prepared from precursor ‘‘b’’ was found to be the catalyst with the lowest activity. A similar observation can be seen in Fig. 3, in which the hydrogenation activity of two

Table 6
Very high maltose feedstock hydrogenation parameters concerning catalyst MRP 9017 at different temperatures and pressures

Catalyst	MRP 9017	MRP 9017	MRP 9017	MRP 9017	MRP 9017	MRP 9017
Feed (g)	600	600	600	600	600	600
Temperature (°C)	100	110	120	130	140	120
Pressure (bar)	40	40	40	40	40	60
Catalyst load (%)	2	2	2	2	2	2
Agitation (rpm)	1400	1400	1400	1400	1400	1400

Note: the pH of the reaction mixture was adjusted to 7 with 0.35 g of $NaHCO_3$.

from precursor “a” prepared ruthenium catalysts are represented. Again, the catalyst supported on peat carbon revealed a lower activity.

Since the ruthenium metal location of both catalysts was the same, i.e. edge, and assuming the Ru dispersion was comparable (due to the same preparation method) the decrease in activity was most likely caused by the peat carbon.

The differences in introducing and/or mixing of the reactants during the catalyst manufacturing from Ru precursor “b” were found to be negligible, see Fig. 4.

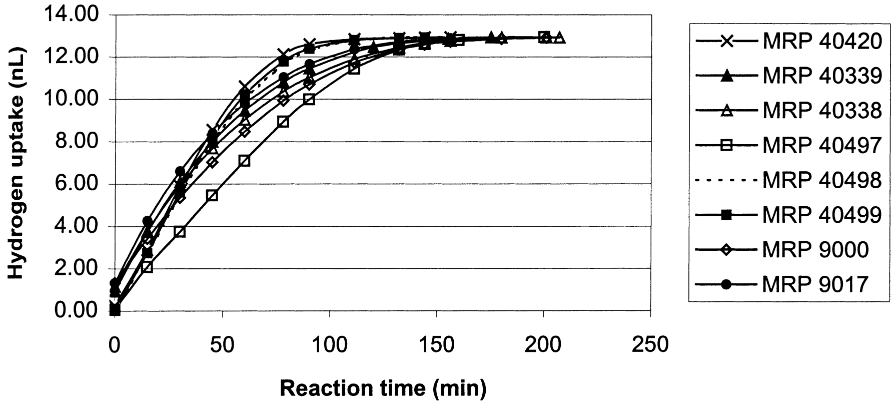

Fig. 2. Dextrose monohydrate hydrogenation activity of all eight tested 5% Ru on carbon catalysts.

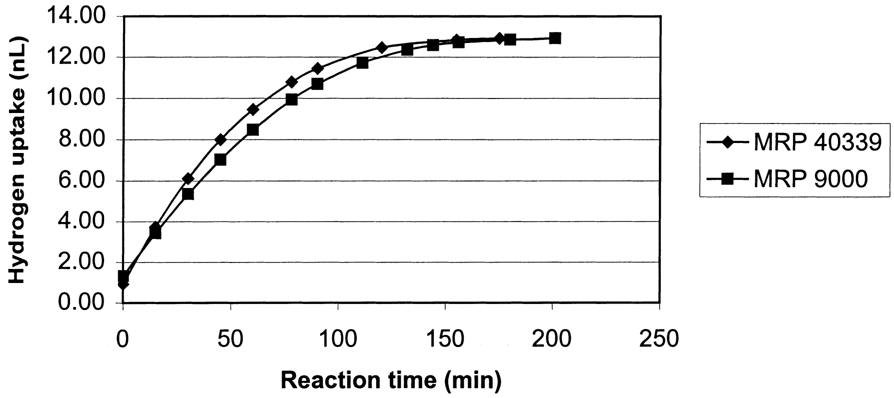

Fig. 3. Dextrose monohydrate hydrogenation activity of two 5% Ru on carbon catalysts, both prepared from the Ru precursor “a” and having an edge metal location. Catalyst MRP 9000 is supported on a peat carbon, whereas catalysts MRP 40339 is supported on a wood carbon.

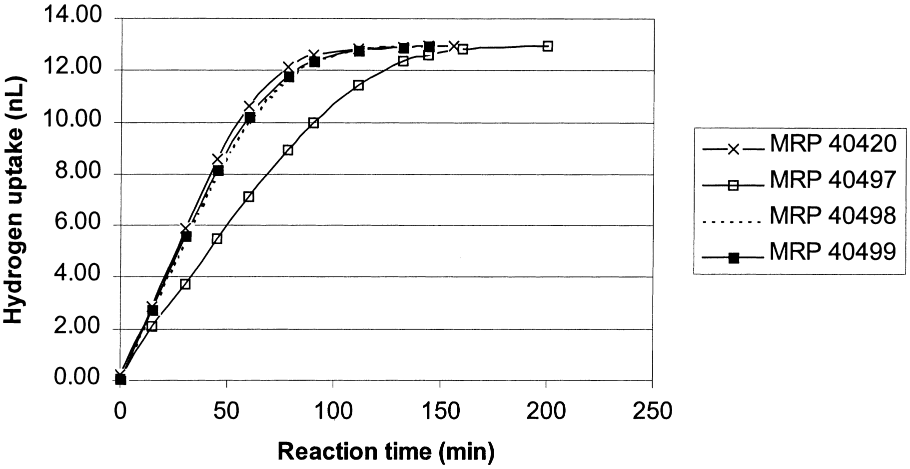

Fig. 4. Dextrose monohydrate hydrogenation activity of four 5% Ru on carbon catalysts, all prepared from Ru precursor "b" and having an edge metal location. Catalyst MRP 40497 is supported on a peat carbon. All other catalysts are supported on the same wood carbon.

As observed from the hydrogenation activities represented in Fig. 5, the ruthenium metal location did not significantly influence the hydrogenation activity of the wood carbon supported catalysts under these reaction conditions.

The product composition of the different runs is represented in Table 7. Sorbitol yields ranged from 97.5 to 99.3%. Some oxidation of glucose to gluconic acid had occurred. The isomerization of glucose to fructose and mannose under the applied hydrogenation conditions was relatively low, as indicated by the low mannitol content.

Comparison of catalyst MRP 9017 and catalyst MRP 40801 showed that the latter catalyst was about twice as active at 120°C and 40 bar H_2 pressure. The edge metal location Ru catalysts, prepared from precursor "b" were found to be more active than a mixed metal location Ru catalyst prepared from precursor "a", see Fig. 6(a). In contrast to what was reported previously concerning catalysts prepared from Ru

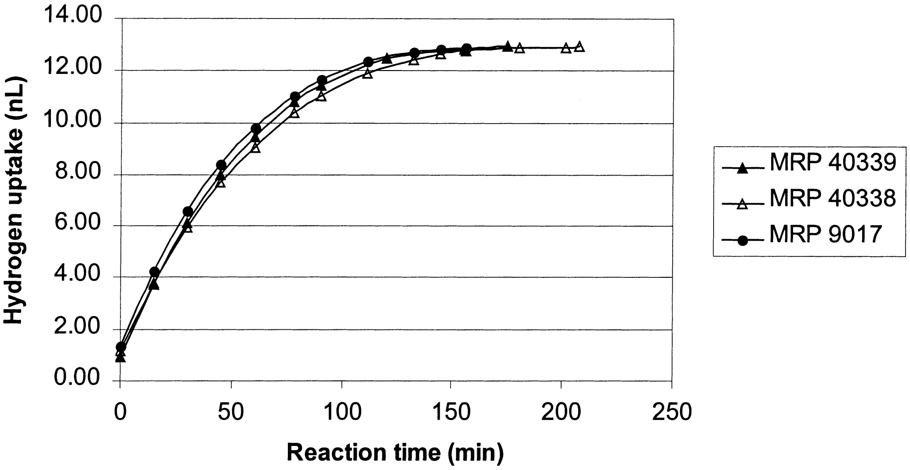

Fig. 5. Dextrose monohydrate hydrogenation activity of three 5% Ru on carbon catalysts, all prepared from Ru precursor "a" on the same wood carbon, but having different metal locations. Catalyst MRP 40339 has an edge metal location, catalyst MRP 40338 has a uniform metal location and catalyst MRP 9017 has a mixed metal location.

Table 7
Dextrose monohydrate hydrogenation results (performed at 100°C 40 bar H_2)

	Catalyst							
	MRP 40420	MRP 40339	MRP 40338	MRP 40497	MRP 40498	MRP 40499	MRP 9000	MRP 9017
Total runtime (min)	156	190	207	200	144	144	201	168
Reducing sugar (%)	0.1	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	<0.1
Composition (%)								
Gluconic acid	n.a.	0.1	0	0.2	0.1	0.1	0.2	0.1
Glucose	0.6	0.2	0.2	0.5	0	0	0	0
Mannitol	1.0	0.5	0.6	1.0	1.0	0.7	0.4	0.5
Sorbitol	97.5	99.2	99.1	98.3	98.2	99.0	99.2	99.3
Others	0.9	0.1	0.1	0.2	0.8	0.3	0.4	0.2

n.a.=not analyzed.

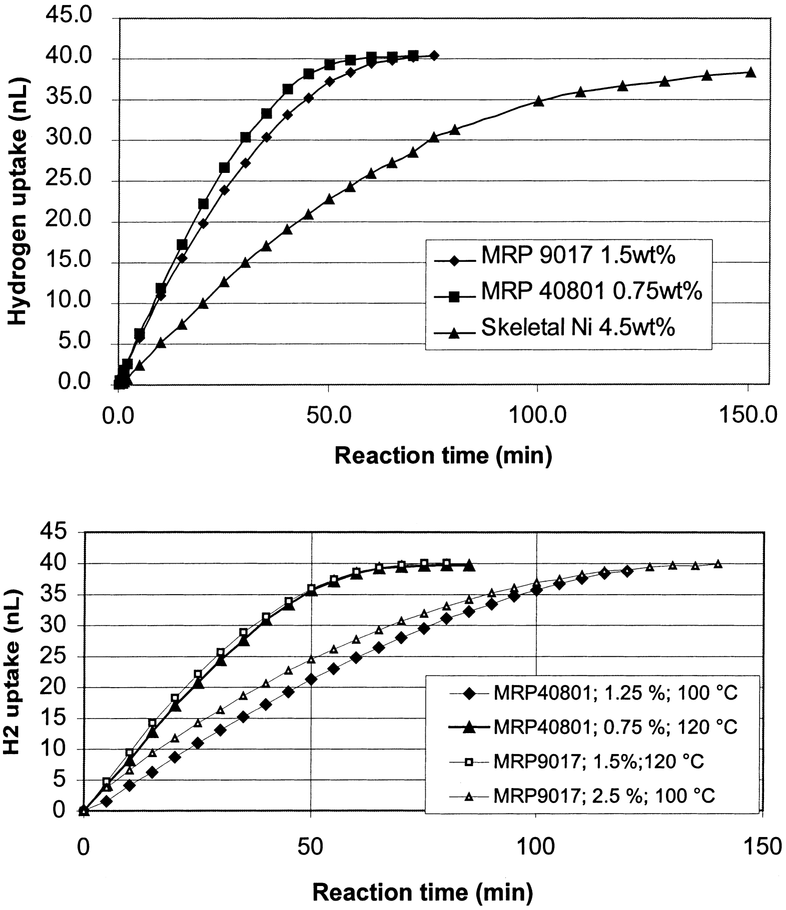

Fig. 6. (a) Dextrose hydrogenation activity of MRP 9017, 40801 and skeletal Ni at 120°C and 40 bar H_2 pressure; (b) Dextrose hydrogenation activity of MRP 9017, 40801 with different catalyst loadings at 100°C and 120°C and 40 bar H_2 pressure.

precursor “a” (see Fig. 5), now the ruthenium metal location influences the hydrogenation activity. Apparently, the application of Ru precursor “b” in the catalyst preparation resulted in a more accessible ruthenium (more edge character of the ruthenium). At 100°C and 40 bar, a similar trend was observed, see Fig. 6(b). The observed hydrogenation rates, calculated out of 15 nl hydrogen uptake time, resembled for the skeletal nickel catalyst (at 4.5 wt% catalyst loading) 0.5 nl H_2/min, for the MRP 9017 catalyst (at 1.5 wt% loading) 1.0 nl H_2/min and for the MRP 40801 (at 0.75 wt% loading) 1.1 nl H_2/min.

The re-usability of the catalysts MRP 9017, 40801 and skeletal Ni are represented in Fig. 7(a), (b) and (c). All catalysts showed good re-usability, however, all hydrogenation rates slowly decreased from the first to the third use.

The sorbitol yield decreased when the hydrogenations were performed at 120°C, see Tables 8–9. Although the pH was kept relatively low, some

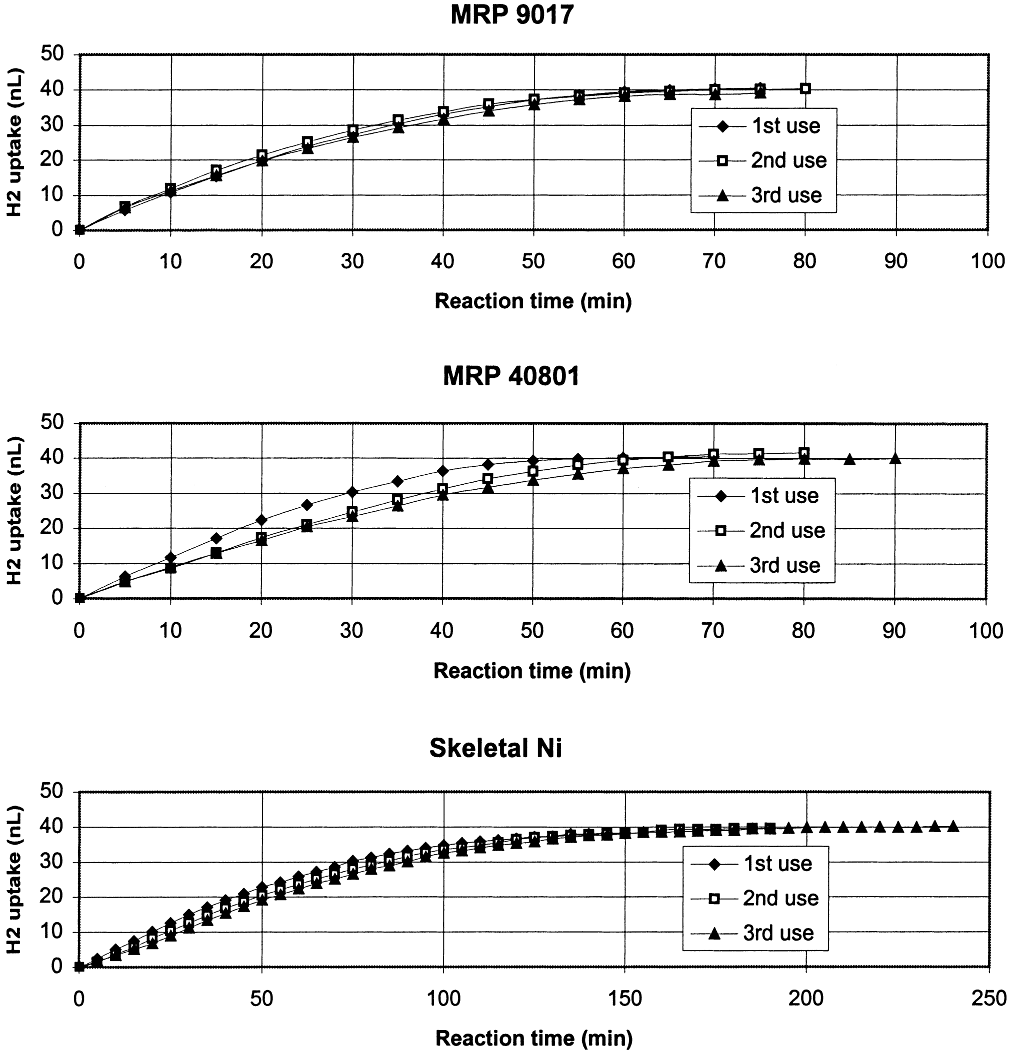

Fig. 7. (a) Hydrogenation activity of the re-use of catalyst MRP 9017; (b) Hydrogenation activity of the re-use of catalyst MRP 40801; (c) Hydrogenation activity of the re-use of skeletal Ni.

Table 8
Dextrose monohydrate hydrogenation test results of re-use and comparison of MRP 9017, 40801 and skeletal Ni at 120°C and 40 bar H_2

	Catalyst								
	MRP 9017	MRP 9017	MRP 9017	MRP 40801	MRP 40801	MRP 40801	Sk Ni	Sk Ni	Sk Ni
Use	1st	2nd	3rd	1st	2nd	3rd	1st	2nd	3rd
Total runtime (min)	80	80	80	70	85	90	150	195	240
pH	4.1	3.6	3.6	3.2	3.1	3.2	3.8	4	3.7
Reducing sugars (%)	0.16	0.16	0.17	0.18	0.16	0.2	0.92	0.59	0.21
Composition (%)[a]									
Maltose	0.1	0.1	0	0.1	0	0.1	0	0	
Glucose	0.3	0.2	0.1	0.2	0.1	0.1	1.7	1.0	
Maltitol	0.7	0.7	0.8	0.6	0.7	0.7	0.2	0.5	
Mannitol	0.8	0.8	0.8	0.9	0.8	0.8	1.2	1.1	
Sorbitol	97.9	98.1	98.1	97.9	98.3	97.9	96.7	97.3	
Iditol	0	0	0	0.3	0.1	0.2	0	0	
Others	0.2	0.1	0.2	0.2	0	0.2	0.2	0.1	

[a] Note: the impurities caused by the application of skeletal Ni contaminated the analytical column. Therefore, several samples were not analyzed.

Table 9
Dextrose monohydrate hydrogenation parameters for comparison of MRP 9017, 40801 at 100°C and 120°C at 40 bar H_2, see also Fig. 6(b)

	Catalyst			
	MRP 40801	MRP 40801	MRP 9017	MRP 9017
Catalyst load (%)	0.75	1.25	1.5	2.5
Temperature (°C)	120	100	120	100
Total runtime (min)	84	120	80	140
Reducing sugar (%)	0.04	1.07	0.06	0.13
Composition (%)				
Glucose	Nd	2.3	0.14	0.24
Maltitol	Nd	0.1	0.16	0
Mannitol	0.42	0.3	0.57	0.36
Sorbitol	98.17	96.3	97.9	98.37
Iditol	1.19	1.0	1.08	0.94
Others	0.22	0.0	0.14	0.09

n.d=not determined.

isomerization of sorbitol to iditol occurred with catalyst MRP 40801. In general, the product formation of both Ru on carbon catalysts were comparable to that of the skeletal Ni catalyst.

3.2. *Very high maltose feedstock hydrogenation*

Hydrogenation of the very high maltose feedstock (at 100°C and 40 bar) resulted mainly in the formation of maltitol and maltotriol, see Table 10. The hydrogenation rates are represented in Fig. 8.

No influence of the carbon support on the hydrogenation rate were observed for catalysts prepared from Ru precursor ‘‘a’’ with an edge Ru metal location, see Fig. 9.

The catalysts prepared from Ru precursor ‘‘b’’ were more active than the catalysts prepared from Ru precursor ‘‘a’’. As shown in Fig. 10, the catalyst supported on peat carbon was found to be less active than the wood supported catalysts. The hydrogenation rates calculated from the time required to consume 2 nl H_2 are represented in Table 10.

The metal location of the ruthenium on wood carbon supported catalysts, prepared from Ru precursor ‘‘a’’ influenced the hydrogenation rate, as shown in Fig. 11.

Table 10
Very high maltose feedstock hydrogenation results

	Catalyst					
	MRP 9017	MRP 40420	MRP 40497	MRP 9000	MRP 40339	MRP 40499
Initial hydrogenation rate (nl H_2/min)	0.034	0.116	0.073	0.042	0.045	0.083
Total runtime (min)	390	180	213	363	360	201
Reducing sugar (%)	1.07	0.03	0.15	0.15	0.22	0.23
Composition (%)						
Maltitol	66.2	68.5	68.4	68.6	69.1	69.1
Maltotriol	21.2	20.8	21	20.9	20.8	20.9
Sorbitol	3.1	2.6	2.5	2.4	2.4	2.4
Others	9.5	8.1	8.1	8.1	7.7	7.6

Variation of the reaction temperature lead to significant changes in hydrogenation rates.

In Fig. 12 the hydrogenation of the very high maltose feed stock with catalyst MRP 9017 at different temperatures is represented. The increase of the temperature had a large effect on the activity of this catalyst system. If we assume that the hydrogen uptake resembles the hydrogenation of maltose, the apparent

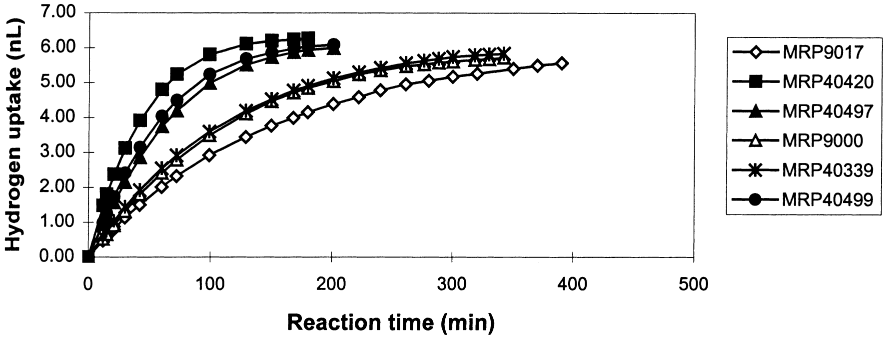

Fig. 8. Very high maltose feedstock hydrogenation activity of all six tested 5% Ru on carbon catalysts.

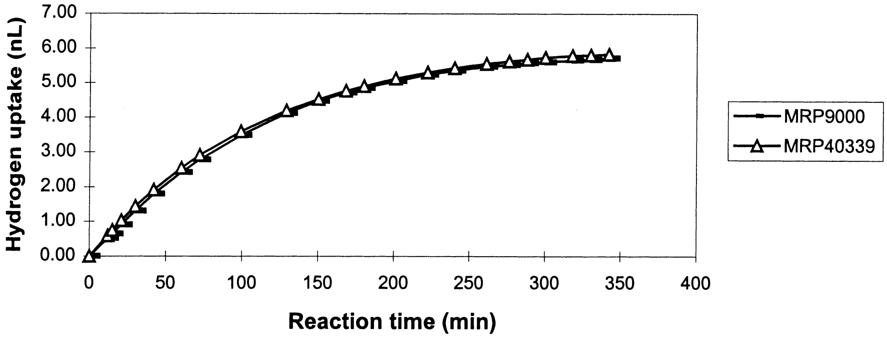

Fig. 9. Very high maltose feedstock hydrogenation activity of two 5% Ru on carbon catalysts, both prepared from the Ru precursor "a" and having an edge metal location. Catalyst MRP 9000 is supported on a peat carbon, whereas catalysts MRP 40339 is supported on a wood carbon.

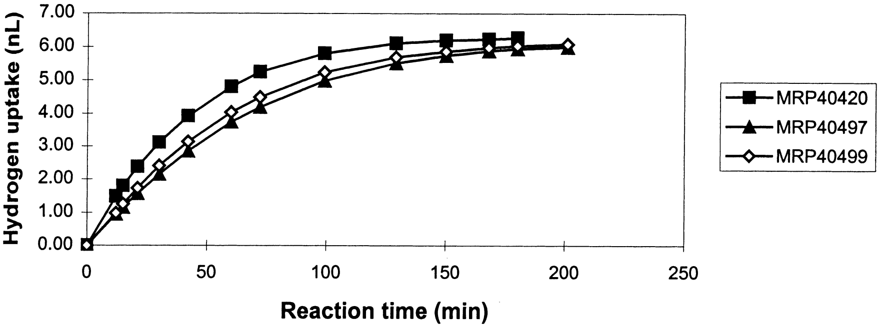

Fig. 10. Very high maltose feedstock hydrogenation activity of three 5% Ru on carbon catalysts, both prepared from Ru precursor "b" and having an edge metal location. Catalyst MRP 40497 is supported on a peat carbon, whereas catalysts MRP 40420 and 40499 are supported on a wood carbon.

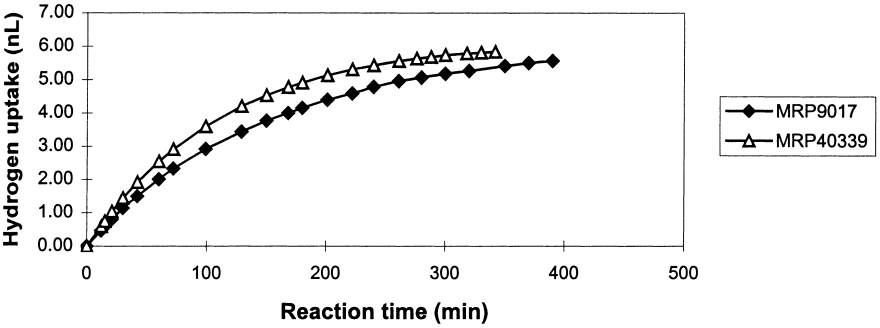

Fig. 11. Very high maltose feedstock hydrogenation activity of two 5% Ru on carbon catalysts, both prepared from Ru precursor "a" on the same wood carbon, but having different metal locations. Catalyst MRP 40339 has an edge metal location, and catalyst MRP 9017 has a mixed metal location.

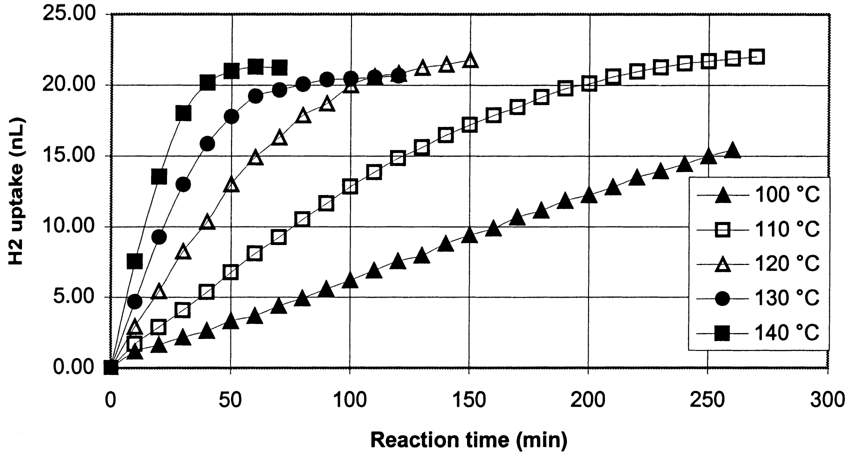

Fig. 12. Hydrogenation of the very high maltose feedstock at 40 bar and different temperatures.

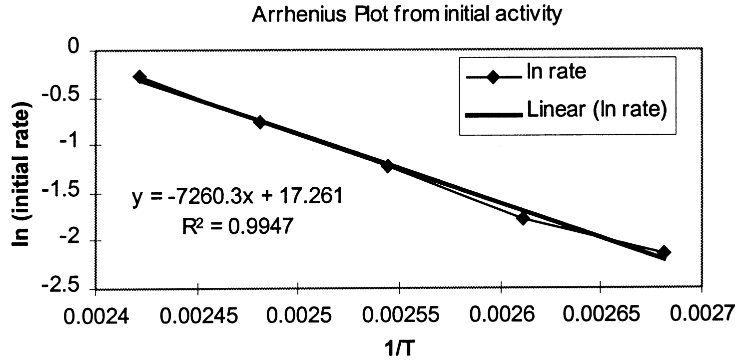

Fig. 13. Arrhenius plot from the initial rates of the reaction (at 10 min). The black line resembles the least square fit.

E_a (activation energy) for this hydrogenation calculated from the Arrhenius plot, see Fig. 13, is about 60.4 KJ/mol.

The change of hydrogen pressure from 40 to 60 bar did hardly influence the hydrogenation activity, as represented in Fig. 14.

4. Conclusions

The glucose and maltose hydrogenation activity of carbon supported ruthenium catalysts depends on the ruthenium precursor which is applied during the preparation of the catalyst. With larger molecules, such as maltose, the metal location of wood carbon supported ruthenium catalysts determines the hydrogenation activity, whereas during the hydrogenation of glucose no effect of the metal location of wood carbon supported ruthenium catalysts is observed.

In general, peat carbon supported catalysts are less active in the hydrogenation of glucose than their corresponding wood carbon analogues. No significant differences in hydrogenation activity of maltose are observed between peat carbon supported or wood carbon supported catalysts. Elevated pressures do not induce a meaningful higher hydrogenation rate of maltose, whereas, elevated temperatures enhance the rate of hydrogenation and by-product formation.

It can be concluded that ruthenium on carbon catalysts are suitable alternatives for skeletal nickel catalysts. The re-use of ruthenium catalysts is at least comparable to that of skeletal nickel catalysts. From

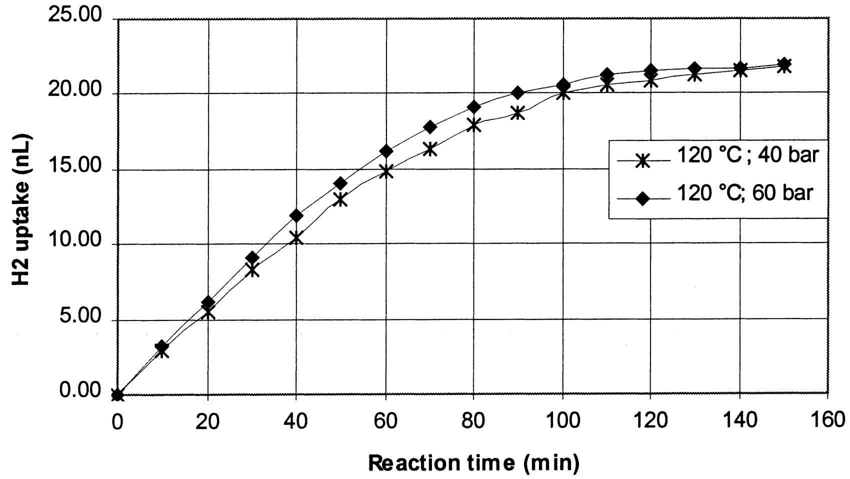

Fig. 14. Hydrogenation of the very high maltose feedstock at 120°C at 40 and 60 bar.

an economical point of view, ruthenium catalysts can be compatible with skeletal nickel catalysts, since they do not require purification of the products. The higher price of a ruthenium catalyst can be overcome due to the regeneration possibilities of the ruthenium catalyst. Hereby the number of re-uses can be enhanced.

As shown in this paper, it is important to optimize the catalyst manufacturing conditions to obtain the best performance in a certain application.

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