Catalysis Today 79–80 (2003) 35–41

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Carbon supported Ru catalysts as promising alternative for Raney-type Ni in the selective hydrogenation of D-glucose

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Abstract

The activity, selectivity and stability of Ru/C catalysts in D-glucose hydrogenation have been compared with those of the conventional catalysts for this process, viz. Raney-type Ni. All catalysts show high selectivity to D-sorbitol (>98%). Promoting Raney-type Ni with Mo and Cr/Fe has a positive effect on the hydrogenation rate. The Cr/Fe promoted system exhibits the highest activity but the Fe leaches from the catalyst into the reaction mixture. Moreover, this catalyst deactivates after successive runs. For all Raney-type Ni catalysts leaching of Ni in the product mixture occurs. Carbon supported ruthenium is an attractive alternative for Raney-type catalysts. The Ru/C catalysts have higher activities, while Ru does not leach. The activity is proportional to the Ru surface area, independent of the preparation method. A novel anionic deposition method renders catalysts with dispersions of 40%.

Keywords: D-Glucose; D-Sorbitol; Ni; Ru; Carbon; Dispersion

1. Introduction

The hydrogenation of D-glucose (dextrose) to D-sorbitol (Fig. 1) is of great industrial importance because D-sorbitol is a valuable additive in foods, drugs, and cosmetics. Moreover, D-sorbitol is an intermediate in Vitamin C production. The most frequently used catalyst for this process is Raney-type Ni, usually promoted with Mo. Excellent settling properties, high activity and low cost price justify the choice for Raney-type Ni. However, during the hydrogenation of D-glucose to D-sorbitol dissolution of nickel occurs. For the food industry the maximum allowable concentration of Ni is 2 mg/kg [1]. As a consequence, purification of sorbitol is necessary and renders this process economically less attractive. The use of ruthenium catalysts could circumvent this problem, since ruthenium is stable against leaching [2,3].

The objective of this work is to assess the applicability of a series of Ru/C catalysts in the hydrogenation of D-glucose to D-sorbitol and to compare its activity, selectivity and stability of Ru/C catalysts with Raney-type Ni, which is currently applied in the industrial production of D-sorbitol. To make a fair comparison promoted Raney-type Ni catalysts were used, since it is known that Mo, Cr and Fe-promoted Raney-type Ni catalysts are more active for D-glucose hydrogenation than unpromoted catalysts [2]. The promoters used in this study were Mo and a combination

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doi:10.1016/S0920-5861(03)00040-3

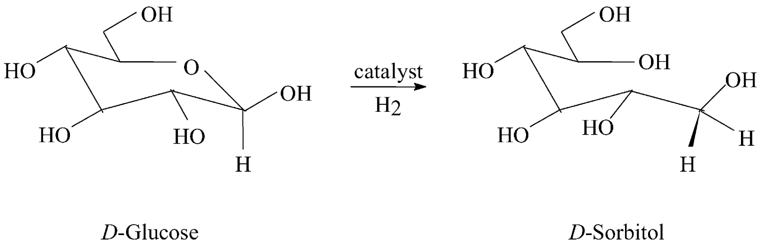

Fig. 1. Hydrogenation of D-glucose.

of Cr and Fe. This latter catalyst is a novel catalyst for this reaction.

2. Experimental

2.1. Materials

The applied skeletal Ni catalysts were provided by Engelhard. Unpromoted as well as promoted (Mo and Cr/Fe) skeletal Ni catalysts were used in this study (see Table 1). Two Ru/C catalysts from Engelhard–Ru/C(1) and (2)–and two homemade Ru/C catalysts–Ru/C(3) and (4)–were used. Activated carbon (CP97, Engelhard) was applied as support material to prepare the homemade Ru/C catalysts. Catalyst Ru/C(3) was prepared by deposition precipitation of $RuCl_3{\cdot}H_2O$, followed by hydrogen reduction. Two grams of carbon support were added instantaneously to an aqueous solution of $RuCl_3$ at 353 K. Ruthenium was precipitated onto the support by drop-wise addition of 1 M sodium hydroxide under vigorous stirring. After completion of the precipitation the solids were filtered, washed with demineralized water until neutrality, dried for 5 h at RT followed by drying at 353 K overnight. The sample was reduced by heating in flowing hydrogen at 2 K/min from RT to 393 K, which was maintained at this temperature for 2 h. Subsequently, it was cooled under flowing nitrogen to RT and then contacted with a mixture of 1% O_2 in N_2 for 12 h. Ru/C(4) was prepared by anionic deposition with $[RuCl_5H_2O]^{2-}$ and reduction in hydrogen. A slurry of 2 g carbon support, 0.6 g $K_2RuCl_5{\cdot}H_2O$ and 50 ml hydrochloric acid solution (0.01 M) was prepared. The suspension was stirred for 6.5 h under reflux conditions and then filtered. The solid was washed with demineralized water until neutrality of the filtrate and dried at room temperature for ca. 8 h and subsequently at 353 K overnight. Catalyst Ru/C(4) was reduced by heating under flowing hydrogen at 1 K/min from room temperature to 413 K, kept at this temperature for 3 h, cooled under Ar, and then contacted with a mixture of 1% O_2 in Ar for 12 h. Table 1 gives the main characteristics of the Ru/C catalysts.

Table 1
Characteristics of the applied catalysts

Catalyst Code	Source	Loading (wt.%)	S_{BET}[a] (m^2/g catalyst)	S_{Ru} (m^2/g catalyst)
Ru/C(1)	Engelhard	4.9 (Ru)	900	6.1
Ru/C(2)	Engelhard	3.5 (Ru)	900	3.1
Ru/C(3)	Dep.-prec.	5.1 (Ru)	900	6.8
Ru/C(4)	Anionic-dep.	5.6 (Ru)	900	8.2
RaNi	Engelhard	–	77	–
RaNi-Mo	Engelhard	2.2 (Mo)	79	–
RaNi-Cr/Fe	Engelhard	2.2 (Cr) 2.2 (Fe)	119	–

[a] S_{BET} is the BET surface area as determined by N_2 physisorption at 77 K.

2.2. Leaching of the catalysts

The amount of metal ions present in the reaction mixture after the hydrogenation run was determined by means of ICP-OES. The analysis was carried out with a Perkin-Elmer 5100PC apparatus. A 10% sorbitol solution was used as a matrix in the calibration samples. All samples were analyzed in duplicate; differences were typically less than 1%.

2.3. Hydrogen chemisorption

The active Ru surface area was determined by means of volumetric hydrogen chemisorption. The

Ru/C catalysts were dried at 393 K followed by reduction at 393 K using a Quantachrome Autosorb-1C. Subsequently, the reaction vessel was evacuated at 393 K and cooled under vacuum. The analysis took place at 308 K. The ruthenium surface area was evaluated from H_2-chemisorption by extrapolation of the total amount of both reversible and irreversible adsorbed hydrogen to zero pressure. The ruthenium surface area was calculated under the assumption that one ruthenium surface atom chemisorbs one hydrogen atom. The obtained results are collected in Table 1.

2.4. Hydrogenation reactions

The catalysts have been screened in a three-phase slurry reactor with a gas-induced stirrer (Premex AG) at 393 K and 4.0–7.5 MPa hydrogen pressure using 10% glucose (0.56 M) in Milli-Q water. The pH was not controlled, but was determined before ($pH = 6$) and after the reaction. The Ru/C catalysts were reduced in situ at 393 K (determined from TPR experiments), 1.0 MPa for 1 h. The Raney-type catalysts were applied as received and were weighted as dry material in an oxygen-free glovebox ($c_{O_2} < 5$ ppm). Above the reactor an injection vessel was situated. The reactor and injection vessels were first purged with N_2 and H_2 at room temperature. When 100 ml of solvent with catalyst was at the desired temperature in the reactor, the injection vessel, containing the concentrated D-glucose solution, was opened. The exact starting time of the reaction could in this way be assured. The temperature, total pressure and the hydrogen consumption were recorded during the reaction. Samples of the product mixture were analyzed with HPLC. The HPLC was equipped with RI detector and separation of the components was achieved by a RCM monosaccharide column operated at 358 K. In a co-study it was already established that the reaction is slightly internal diffusion limited at the applied conditions for the most active catalyst, Ru/C(4) [4]. The internal effectiveness factor η, as calculated from the Wheeler–Weisz parameter, was determined to be 0.91. To study the stability of the Raney-type Ni catalyst promoted with Cr/Fe five consecutive hydrogenation runs were performed. After each run the reactor was emptied under hydrogen atmosphere. The catalyst was washed in situ with 150 ml water and a fresh reaction mixture was introduced again for the following run. In this procedure it was assured that the catalyst was not exposed to air.

3. Results and discussion

3.1. Raney-type Ni

All catalysts show a high selectivity to D-sorbitol (>98%). Main by-products during reaction are fructose and mannitol due to isomerization of glucose and sorbitol, respectively. The catalytic hydrogenation of D-glucose can usually be described by Langmuir–Hinshelwood kinetics with a transition from zero-order dependency in D-glucose at high concentrations to first-order behavior at low concentrations [4]. At the applied D-glucose solutions (10 wt.%) in this study, the reaction is first-order in D-glucose for all catalysts (Fig. 2). The activities of the Raney-type Ni catalysts are therefore expressed by the pseudo first-order reaction rate constants ($kg^{-1}\,s^{-1}$ catalyst) and are plotted in Fig. 3. The promoters have a beneficial effect on the reaction rate of Raney-type Ni. The Cr/Fe promoted Raney-type Ni performs better than the RaNi-Mo catalyst, which is the traditional catalyst used in this process. It is believed that upon adsorption of D-glucose on metals an ionized species is generated which is susceptible to attack by hydrogen [5]. Since electron affinity increases from $Fe < Cr < Mo < Ni$ [6], this could explain the enhancement of the reaction rate by the promoters. The promotor atoms are more electropositive than Ni and act as adsorption sites for D-glucose. The catalyst surface area increases significantly when Cr and Fe are introduced to the Ni catalyst (Table 1). But even when the performance of catalyst is normalized to its surface area, the promoted systems still exhibit an enhanced activity. In the pressure range tested (4.0–7.5 MPa) the reaction was first-order in hydrogen for the Mo promoted RaNi (Fig. 4), which is generally observed in the catalytic hydrogenation of D-glucose to D-sorbitol in this pressure range [4,7].

Since the hydrogenation mixture after each run is slightly acidic ($pH = 5$) due to the formation of small quantities of gluconic acid, atoms tend to leach from the catalyst surface into the liquid phase. This phenomenon is highly undesirable, because of the resulting impurities in the product and, moreover,

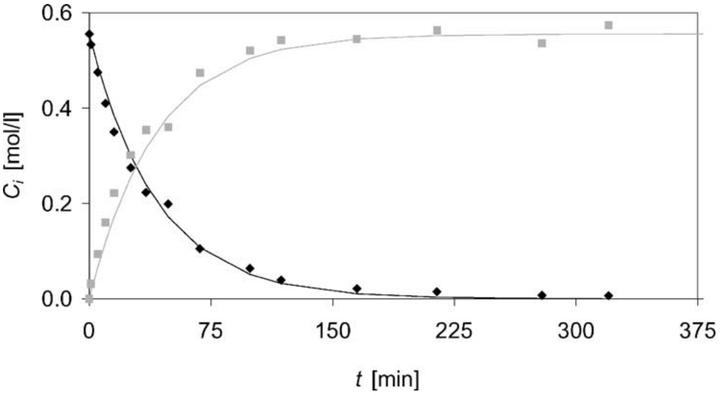

Fig. 2. Typical concentration profile of the hydrogenation of D-glucose to D-sorbitol (RaNi, 4.0 MPa, 393 K, 10% glucose). (◆) Glucose, (■) sorbitol; the lines represent a first-order fit.

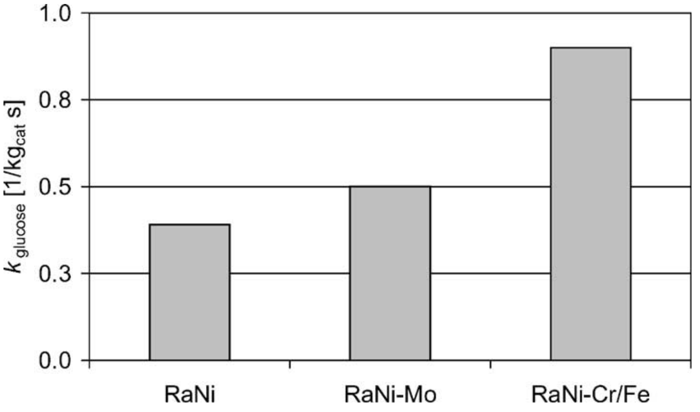

Fig. 3. Activity of the Raney-type Ni catalysts at 4.0 MPa, 393 K and 10 wt.% D-glucose.

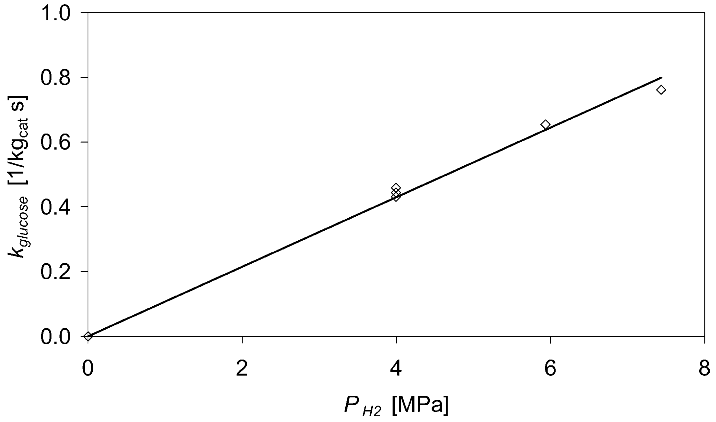

Fig. 4. The influence of hydrogen pressure on the activity (RaNi-Mo, 393 K, 10 wt.% D-glucose).

Table 2
Amount of leached metal ions (%)[a]

	Ni	Al	Mo	Fe	Cr	Ru
RaNi	0.8	0.8	–	–	–	–
RaNi-Mo	0.6	0.5	0.0	–	–	–
RaNi-Cr/Fe	1.1	1.5	–	27.7	1.2	–
Ru/C(2)	–	–	–	–	–	0.0

[a] Relative to starting catalyst material.

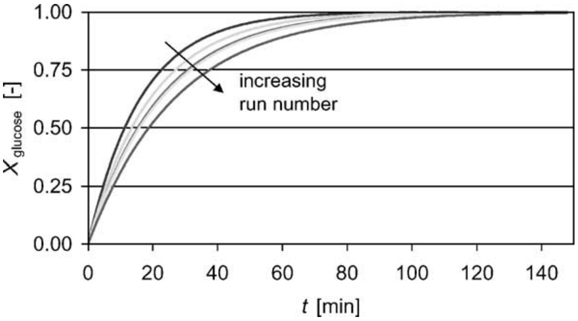

Fig. 5. Conversion of glucose as function of time in five successive hydrogenation runs for RaNi-Cr/Fe (4.0 MPa, 393 K and 10 wt.% D-glucose).

loss of active catalyst sites. Gallezot et al. studied the effect of promoters on the stability of Raney-type Ni catalysts [6,8]. It was found that iron promoted Raney-type Ni showed deactivation after successive runs due to leaching of the iron from the Ni surface. Leaching of molybdenum or chromium was less pronounced. The combined action of Cr and Fe was not studied. In this study, the amount of dissolved metal ions in the reaction mixture after each hydrogenation run was determined and given in Table 2. It can be seen that Ni has leached from the catalyst surface for all Raney-type Ni catalysts. For the Cr/Fe promoted catalysts around 1 wt.% of the Ni leaches from the catalyst (ca. 350 mg/kg sorbitol). This is most likely caused by complexation of products with Ni ions from the catalyst surface [9]. Table 2 indicates furthermore that addition of Mo stabilizes the Ni in the catalyst. Mo does not leach at all, whereas Cr leaches a little. Fe dissolves quite easily in the reaction mixture, in agreement with Gallezot et al. This can be explained by the fact that Fe is less noble. This leaching of Fe suggests that the activity of the catalyst is likely to decrease in time. The deactivation of RaNi-Cr/Fe was studied because it is the most active Raney-type Ni catalyst (Fig. 5). The five runs show a steady decrease in activity. After five consecutive runs 40% of the initial activity is lost. Fig. 6 shows the loss in activity during the stability tests as a function of iron content in the catalyst. Initially a large amount of Fe is lost (almost 30%), whereas only 10% loss in activity is observed. After run 3 the decrease in hydrogenation activity is proportional to the decrease in Fe content. This observation suggests that the fresh catalyst contains a significant amount of Fe, which has only a limited effect on the catalytic performance, most likely in the shape of bulk Fe. After two runs this bulk Fe has been leached into the reaction mixture and from that moment the Fe removed leads to a decrease in activity. To investigate the influence of the Fe on the activity further, also a pre-leached Raney-type Ni-Cr/Fe catalyst was prepared by treatment in 0.01 M HCl under reflux conditions. Whereas after this treatment hardly any Cr, Ni and Al was leached, about 14% of the Fe was removed from the catalyst. The activity was only slightly lowered (see Fig. 6), in agreement with the stability experiment.

3.2. Carbon supported Ru catalysts

The activities of the applied Ru/C catalysts are shown in Fig. 7. The selectivity to sorbitol was >98% in all cases. Since the acidity is an important factor in glucose hydrogenation, the pH was measured before and after reaction. For the Ru/C catalysts no significant difference with the RaNi samples was observed; for all catalysts the pH was slightly lowered after reaction to about pH = 5. All Ru catalysts are at least two times more active than the Ni catalysts per kg of

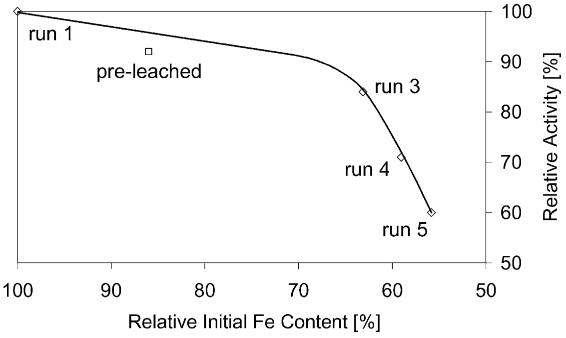

Fig. 6. Relation between leached Fe and catalytic activity after each hydrogenation run relative to starting conditions. The pre-leached sample is indicated with (□).

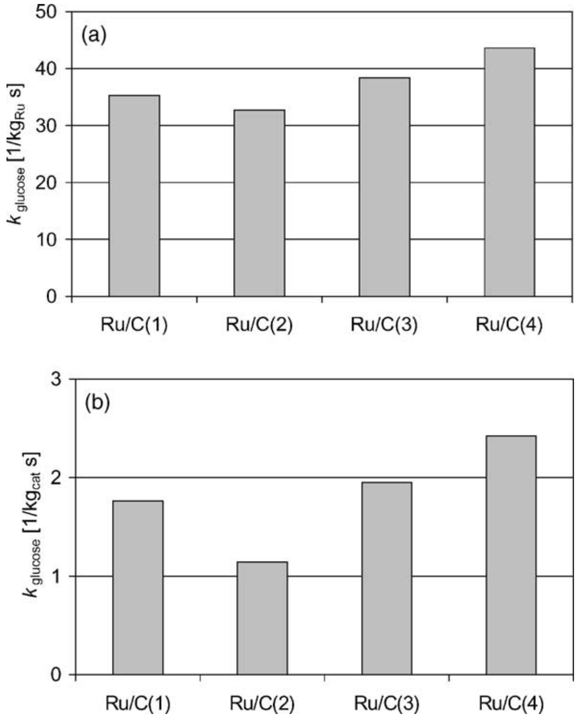

Fig. 7. Activity of the Ru/C catalysts: (a) expressed per kg of Ru; (b) expressed per kg of catalyst (4.0 MPa, 393 K and 10 wt.% D-glucose).

catalyst. Comparing the activity per kg of active metal (pseudo first-order reaction rate), the Ru/C are even more efficient, since the Raney-type nickel catalysts consist of pure metal. The carbon supported Ru catalysts exhibit comparable activity per kg of Ru, independent of the preparation procedure. The activity of the commercial Ru/C(1) catalyst has also been tested by Van Gorp et al. [3]. The tests were performed at identical temperature and hydrogen pressure, but with a 2.78 mol/l D-glucose solution instead of the present 0.56 mol/l solution. A first-order reaction rate of 0.22 (1/s kg catalyst) was found, which is eight times lower than the value found in this work. Most likely, these data were disguised by severe mass transfer limitations of hydrogen [4]. In Fig. 8 the reaction rate constants are plotted against the active Ru surface areas, representing the metal dispersion. The reaction rate is clearly proportional to the metal surface area. The anionic deposition method renders catalysts with the highest dispersion. A study on the kinetics of this reaction on Ru/C is in progress [4].

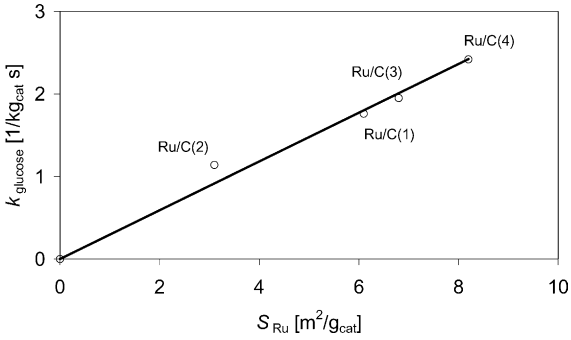

Fig. 8. Activity for glucose hydrogenation vs. Ru metal surface area for different types of Ru/C catalysts.

Ruthenium does not leach from the carbon support at the applied conditions, as can be concluded from Table 2. This was also shown by Gallezot et al. [2]. In this perspective Ru/C catalysts are a better option than Raney-type Ni. Combined with the high activity, Ru/C is a promising alternative for Raney-type catalysts in industrial D-glucose hydrogenation. It should however be confirmed whether the Ru/C catalysts are stable in time.

4. Conclusions

In this preliminary study it was shown that the catalytic hydrogenation of D-glucose to D-sorbitol is highly selective for all catalysts investigated and can be described by pseudo first-order kinetics for the operating conditions studied. Promoting Raney-type Ni with Mo and Cr/Fe has a positive effect on the hydrogenation of D-glucose. The Cr/Fe promoted system exhibits the highest activity but the Fe leaches severely from the catalyst into the reaction mixture. Moreover, this catalyst deactivates after successive runs. Carbon supported ruthenium seems to be an attractive alternative for Raney-type catalysts. The Ru/C catalysts display higher activities and Ru does not leach into the reaction solution. Applying the described preparation methods, Ru/C catalysts can be produced, which exhibit comparable or better performances than the commercial samples. The activity of Ru/C catalysts is proportional to the Ru metal surface area, independent of the preparation procedure. The anionic deposition method renders catalysts with the highest dispersion.

Acknowledgements

This work has been supported by the Netherlands Foundation for Technical Research, STW, and forms part of a project initiated by Delft University of Technology, Engelhard and DSM. We thank J.C. Groen (DUT, PAS&BR) for performing the H_2-chemisorption measurements. K. Bayense (Engelhard de Meern) is acknowledged for the stimulating discussions.

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