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Structure sensitivity in catalytic hydrogenation of glucose over ruthenium

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ABSTRACT

The structure sensitivity was studied in the hydrogenation of glucose to sorbitol over supported ruthenium catalysts in a semi-batch reactor. Ruthenium on carbon supports with different ruthenium particle sizes was prepared and evaluated in the hydrogenation experiments. The highest turnover frequency was obtained with a catalyst bearing average ruthenium particle size of ca. 3 nm.

1. Introduction

Hydrogenation of glucose to sorbitol is an important industrial process. Sorbitol can be used as an alternative sweetener in food, intermediate in pharmaceutical production and as a humectant in cosmetics. Hydrogenation of glucose or other sugars to corresponding sugar alcohols can be performed over nickel and ruthenium catalysts as well as other metals belonging to the platinum group. Typically Raney-type Ni catalysts are used in the industrial production of sorbitol from glucose [1–3]. The main reason for using nickel in industry is the low costs. However, there are some disadvantages in using nickel as a hydrogenation catalyst. It has been found that nickel deactivates through a loss of active surface (sintering), leaching of nickel into the reaction mixture and poisoning [1–3]. Leaching of nickel into the sorbitol solution increases the purification costs since nickel is toxic. These drawbacks can be overcome by using a different catalyst, for instance ruthenium supported on carbon. Glucose hydrogenation to sorbitol over ruthenium catalysts has been extensively investigated [3–7]. Despite the large number of publications on hydrogenation over ruthenium catalysts, no reports on the effect of ruthenium particle size could be found in the open literature. The structure sensitivity can be investigated by plotting the turnover frequency (TOF) as a function of the particle size. The TOF can be declining as in oxidation of glycerol [8], increasing until reaching a plateau as in Fischer–Tropsch synthesis [9] or constant. However, interesting reports on reactions where the TOF goes through a maximum can be found in the open literature. These reactions include hydrogenation of crotonaldehyde [10] and ethene [11], oxidation of methane [12], deoxygenation of palmitic and stearic acids [13] on different metals other than ruthenium. The selectivity to cinnamyl alcohol in the hydrogenation of cinnamaldehyde over ruthenium increased over larger ruthenium particles supported on carbon, while the specific activity expressed per exposed ruthenium atoms remained constant [14].

In this work, the influence of ruthenium nanoparticle size on the catalyst activity for glucose hydrogenation is investigated. For this purpose, ruthenium on carbon catalysts with ruthenium particle sizes ranging from 1 to 10 nm were synthesized and tested.

2. Materials and methods

2.1. Ruthenium on carbon catalysts

Several different ruthenium on carbon catalysts were studied in this work. Both commercial and in-house prepared catalysts were tested and compared.

The commercial samples were a 4.6% ruthenium on activated carbon (AC) catalyst and a 0.7% ruthenium on carbon extrudates catalyst, denoted as Catalysts A and B. Prior to the experiments the Catalyst B was crushed and sieved to a fraction smaller than

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125 μm. The in-house prepared catalysts were made by deposition of ruthenium on activated carbon, carbon nanotubes (CNT), and on nitrogen doped carbon nanotubes (NCNT). The catalyst samples were not separately reduced under hydrogen before the hydrogenation experiments. However, heating of the reactor and the catalyst was done in hydrogen atmosphere.

2.1.1. Catalyst C

The deposition of ruthenium on the activated carbon was performed by precipitation of [$RuCl_3 \cdot HCl$] with NH_4OH, followed by reduction of ruthenium hydroxychloro-complexes by $NaBH_4$.

2.1.2. Catalyst D

CNTs were used as catalyst support materials in the preparation of Catalyst D. Before deposition of ruthenium the CNTs were oxidized by treatment with concentrated HNO_3 (70%, Aldrich) in order to increase the hydrophilicity by introduction of surface carboxylic groups [15]. Ruthenium(IV) oxide was precipitated on the oxidized CNT according to the method described by Fu et al. [16]: 30% H_2O_2 (Aldrich) aqueous solution was added dropwise to a stirred mixture of $RuCl_3 \cdot H_2O$ (40.9%, Haereus) and oxidized CNT in water. The rate of addition was controlled to keep the temperature of the reaction mixture ≤60 °C. After completed addition the mixture was stirred at 80 °C for additional 3 h. After cooling to room temperature the Ru/CNT material was filtered and repeatedly washed with water and dried at 100 °C in an oven overnight.

2.1.3. Catalyst E

NCNT support material was prepared as described elsewhere [17]. Ruthenium was deposited on NCNT adapting the method of Fu et al. [16] outlined above.

2.1.4. Catalyst F

The Catalyst F was prepared in a three step procedure. In the first step NCNTs were suspended in a solution of polyvinylpyrrolidone (PVP) (58 000 g/mol, ABCR) in ethanol (Aldrich) and the mixture was sonicated for 2 h. Then, the solid material was filtered off, repeatedly washed with ethanol and dried in an oven at 100 °C. The pretreated support material was mixed with an aqueous solution of $RuCl_3$, sonicated for 2 h and stirred 4 h at room temperature. Finally, after complete evaporation of the water, the (pre-) catalyst was reduced by heating the NCNT-PVP-$RuCl_3$ solid mixture at 195 °C in excess of ethylene glycol (Aldrich) during 2 h.

2.1.5. Catalyst G

A NCNT-PVP-$RuCl_3$ mixture was analogously prepared as described for Catalyst F. After drying the impregnated support, it was put into a tube furnace and a flow of Ar (5.0 Linde) (80 ml/min, 30 min) was passed over it at room temperature in order to remove air from the tube. Reduction was performed applying a mixture of Ar/H_2 (5.0 Linde) (H_2 20 ml/min; Ar 80 ml/min), while the temperature was increased to 450 °C by applying a 3 °C/min heating rate. After reaching 450 °C, the temperature was maintained for another 4 h.

2.1.6. Catalyst H

Catalyst H was prepared by a similar method as applied for Catalyst G, but a different procedure was applied for reduction in order to obtain larger ruthenium nanoparticles. A NCNT-PVP-$RuCl_3$ mixture was analogously prepared as described for Catalyst F and the catalyst precursor placed into a tube furnace. In the air atmosphere, the temperature was raised by 3 °C/min to 300 °C, kept at 300 °C for 2 h. Then a flow of Ar (80 ml/min, 30 min) was used to remove air from the tube. Subsequently, a mixture of Ar/H_2 (H_2, 20 ml/min; Ar, 80 ml/min) was applied. The temperature was raised to 450 °C at a 3 °C/min heating ramp and was kept during 8 h.

2.2. Catalyst characterization

Ruthenium content in the solid catalysts was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Spectro ICP spectrometer (Model: Arcos) at a mean wavelength of Ru, which was determined from the following three wavelengths of Ru: 240.272 nm, 267.876 nm, 245.553 nm.

The size and size distributions of the ruthenium nanoparticles were measured by transmission electron microscopy (TEM). TEM measurements were performed with a FEI TECNAI 20 electron microscope operated at an acceleration voltage of 200 kV. LaB6 was used as the electron source. Digital images were taken with a side mounted CCD camera (Olympus, MegaView III). For TEM preparation a few milligrams of each sample were ultrasonicated in 2 ml of ethanol during 15 min and a drop of this dispersion was placed on a 300 mesh holey carbon coated copper TEM-grid (plano S147-1). The mean sizes of Ru particles were estimated from TEM micrographs by single particle measurement of at least 140 particles. The dispersion of the ruthenium nanoparticles was also determined by CO chemisorption with a Micromeritics AutoChem 2910. A ratio of CO:Ru = 1:1 was used in the calculations. Prior to the measurement the sample was reduced under hydrogen flow at 300 °C.

2.3. Hydrogenation reactor set-up

Hydrogenation of glucose over different ruthenium on carbon catalysts was investigated in a Parr 4561 autoclave (300 ml). The autoclave was equipped with a gas entrainment impeller, baffles, heating jacket and a cooling coil, sampling line, pressure, temperature and stirring rate controllers. The glucose solution was pre-heated and saturated with hydrogen in a separate chamber. The catalyst sample was put in the reactor which was flushed with nitrogen and hydrogen before heating. When the temperature was 120 °C the glucose solution was fed to the reactor and the pressure was increased to 19 bar of hydrogen. Samples (1–2 ml) were periodically withdrawn through a 0.5 μm sinter during the semi-batch experiments. A constant 19 bar hydrogen (5.0, AGA) was applied by controlled addition and the reaction temperature was 120 °C. A 0.1 mol/L 120 ml glucose (Fluka, ≥98% purity) solution was used. The stirring rate was 1000 rpm. The experiments were carried out between 120 and 180 min and the amount of catalyst was between 0.1 and 0.2 g.

The pH of sugar and the catalyst slurry was measured for some cases being for example equal to 6.7 for Catalyst A. It is well known that isomerization of glucose to fructose can occur at much higher alkaline pH (ca. 12–13) as demonstrated in [18]. Such isomerization leads to subsequent hydrogenation of fructose forming mannitol and sorbitol [19]. Much milder conditions in the present work did not thus result in formation of fructose, mannitol and degradation products.

2.4. Glucose and sorbitol analysis

The concentrations of glucose and sorbitol were determined by high-performance liquid chromatography (HPLC) (HITACHI Chromaster HPLC) equipped with an RI detector. A Biorad HPX-87C carbohydrate column was used, the mobile phase was 1.2 mM $CaSO_4$. The temperature of the column was 70 °C and the flow rate of the mobile phase 0.5 ml/min, the detector was at 40 °C. Calibrations were made for glucose and sorbitol. The by-products, mannitol and glycerol, were also analyzed by HPLC.

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Table 1
Catalyst characterization results.

Catalyst sample	Support	Ru loading (wt%)	Ru particle size (nm)
Catalyst A	AC	4.6	2.5 (CO)
Catalyst B	AC	0.7	2.9 (CO)
Catalyst C	AC	2.0	10.0 (CO)
Catalyst D	CNT	3.3	1.3 (TEM)
Catalyst E	NCNT	3.6	1.2 (TEM)
Catalyst F	NCNT	4.1	1.5 (TEM)
Catalyst G	NCNT	3.6	3.3 (TEM)
Catalyst H	NCNT	3.4	5.3 (TEM)

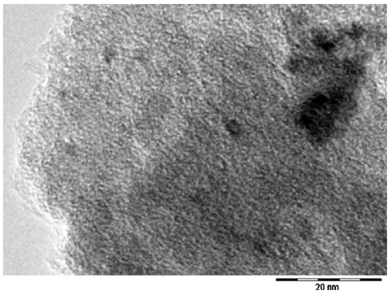

Fig. 1. TEM image of Catalyst A, ruthenium particle size 2.5 nm.

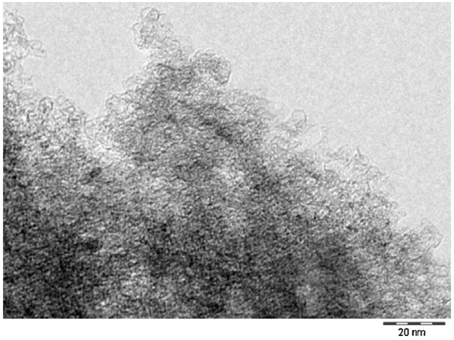

Fig. 2. TEM image of Catalyst B, ruthenium particle size 2.9 nm.

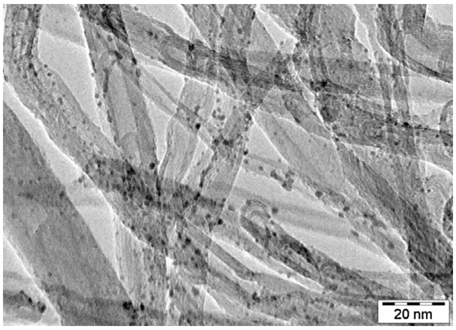

Fig. 3. TEM image of Catalyst D, ruthenium particle size 1.3 nm.

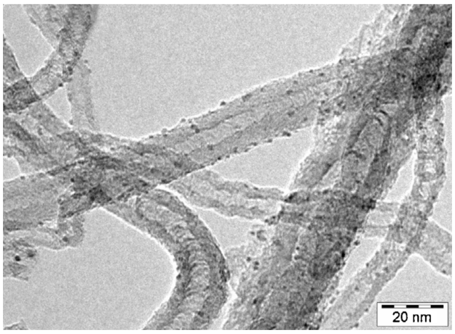

Fig. 4. TEM image of Catalyst E, ruthenium particle size 1.2 nm.

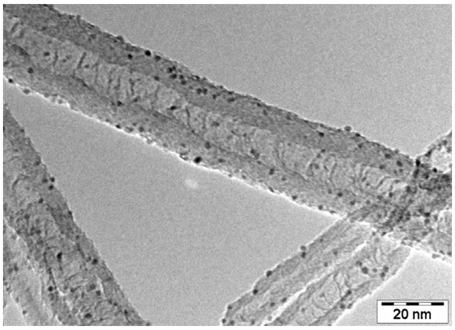

Fig. 5. TEM image of Catalyst F, ruthenium particle size 1.5 nm.

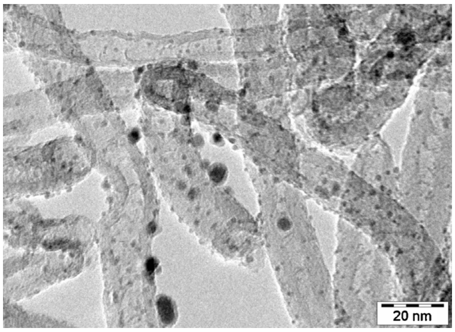

Fig. 6. TEM image of Catalyst G, ruthenium particle size 3.3 nm.

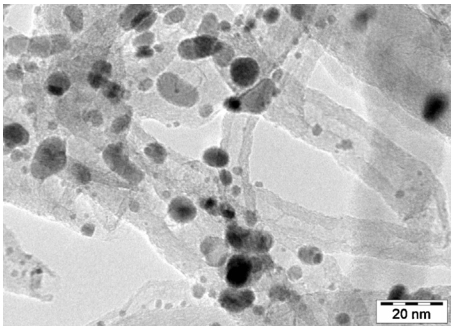

Fig. 7. TEM image of Catalyst H, ruthenium particle size 5.3 nm.

3. Results and discussion

3.1. Catalyst characterization results

The ruthenium content and average particle size of the catalysts are listed in Table 1. TEM images of the samples are shown in Figs. 1–7.

3.2. Glucose hydrogenation results

The glucose conversion as a function of reaction time multiplied by the amount of ruthenium in the reactor is displayed in Fig. 8. The screened catalysts showed different behavior in terms of activity. Full conversion was achieved in most cases, although some

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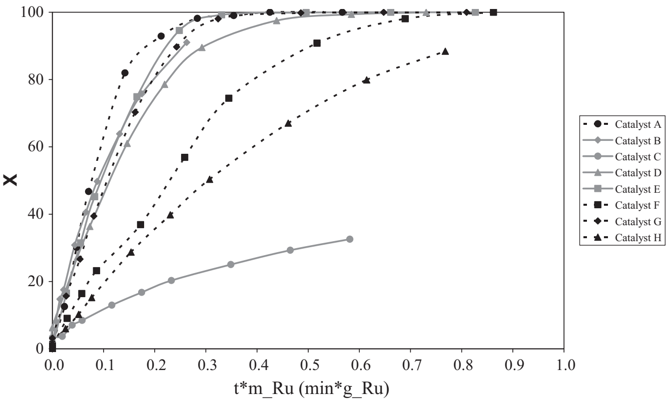

Fig. 8. Conversion vs. reaction time multiplied by the amount of ruthenium in the reactor.

Table 2
Selectivity (%) to sorbitol over the screened catalysts.

Catalyst	Selectivity
Catalyst A	96.1
Catalyst B	95.5
Catalyst C	28.8
Catalyst D	87.6
Catalyst E	94.9
Catalyst F	92.1
Catalyst G	92.4
Catalyst H	89.0

catalysts displayed lower activity, i.e. Catalyst C. The duration of the experiments was between 120 and 180 min.

The highest activities were observed for Catalysts A, B and G supported respectively on active carbon and NCNT bearing the metal cluster size close to 3 nm.

Selectivity to sorbitol is listed in Table 2. High selectivities, up to 96.1%, at full conversion were achieved with most of the catalysts. Inferior selectivity in terms of hydrogenation was obtained with Catalyst C, which in fact was very active in hydrogenolysis, resulting in glycerol as the main product.

Leaching of ruthenium was investigated by ICP, the concentration of Ru was below the limit of quantification meaning than in the worst case only 0.05 mg/L of ruthenium could be present in the liquid after the reaction. This value corresponds to maximum ruthenium leaching of 0.13%, in practice it can be even smaller.

3.3. *Structure sensitivity*

Utilization of different catalysts with different ruthenium nanoparticle sizes made it possible to study the influence of the average particle diameter on the catalytic activity. The different carbon supports used should be inert in the hydrogenation of glucose, therefore the catalytic activity should only depend on the properties of the ruthenium.

The activity of the different catalysts was calculated based on the initial glucose 50% conversion rates and divided by the amount of exposed ruthenium. The amount of exposed ruthenium was calculated from on the average particle size, which was determined by TEM analysis or CO chemisorption.

Analysis of structure sensitivity is also founded on the average ruthenium particle size, not considering particle morphologies or size distribution. The model presented below assumes that ruthenium particles are cubo-octahedral in symmetry.

For such shape of nanoparticles the fraction of edges to the total number of atoms on the surface, which besides edges also includes square and triangular faces, is given by [20]

$$f_{edges} = \frac{N_{edges}}{N_{edges} + N_{square\_faces} + N_{triangular\_faces}} \tag{1}$$

The fraction of edges can be described in a simplified way as $f_{edges} \approx 1/d_{cluster}$ when d is given in nm [21].

It was previously shown [21] that the rate constants of adsorption and desorption are given respectively by

$$k_{ads} = k'_{ads} e^{[-\alpha f_{edges}(\Delta G_{ads,edges} - \Delta G_{ads,terraces})]/RT};$$
$$k_{des} = k'_{ads} e^{[(1-\alpha) f_{edges}(\Delta G_{ads,edges} - \Delta G_{ads,terraces})]/RT} \tag{2}$$

where α is the Polanyi parameter and $\Delta G_{ads,edges}$ corresponds to adsorption on edges. Eq. (2) in combination with (1) gives a possibility to describe turnover frequency dependencies on cluster size for different reaction mechanisms.

When hydrogenation kinetics follows Langmuir–Hinshelwood type of mechanism with noncompetitive adsorption of hydrogen and the organic substrate the reaction rate per exposed site is expressed by

$$v = \frac{k K_G C_G K_{H_2} C_{H_2}}{(1 + K_G C_G)(1 + K_{H_2} C_{H_2})} \tag{3}$$

where k is the rate constant, K_G and K_{H_2} are the adsorption coefficients and C_G and C_{H_2} the concentrations of glucose and hydrogen, respectively. Based on the previous considerations [21] for Langmuir–Hinshelwood kinetics the rate expression for turnover frequency can be described as

$$\mathrm{TOF} = \frac{k e^{\alpha(\chi_G + \chi_{H_2})/d_{cluster}} K_G C_G K_{H_2} C_{H_2}}{(1 + K_G e^{\chi_G/d_{cluster}} C_G)(1 + K_{H_2} e^{\chi_{H_2}/d_{cluster}} C_{H_2})} \tag{4}$$

where α is the Polanyi parameter for the surface reaction between adsorbed sugar and hydrogen and parameters x account for differences in the Gibbs energy of adsorption on edges and terraces respectively for hydrogen and glucose

$$\chi_G = \frac{(\Delta G_{ads,edges,G} - \Delta G_{ads,terraces,G})}{RT};$$
$$\chi H_2 = \frac{(\Delta G_{ads,edges,H_2} - \Delta G_{ads,terraces,H_2})}{RT} \tag{5}$$

Hydrogenation of sugars over ruthenium is often described by zero order kinetics at high hydrogen pressures [22], thus allowing to simplify Eq. (5)

$$\mathrm{TOF} = \frac{k e^{\alpha \chi_G/d_{cluster}} K_G C_G}{(1 + K_G e^{\chi_G/d_{cluster}} C_G)} \tag{6}$$

The structure sensitivity of glucose hydrogenation is illustrated in Fig. 9 including also comparison of the experimental and calculated values. A clear maximum in Fig. 9 indicates that glucose hydrogenation is a structure sensitive reaction and that an optimal catalyst should contain ruthenium particles around 3 nm in size. Catalyst C was excluded from the data fitting since it gives mainly other products. It should be also noted that even if only the catalysts prepared on the carbon nanotubes are taken into account one could still see the effect of structure sensitivity with a maximum in the TOF plot at slightly larger particle size than what is reported now when also some active carbon supported catalysts are considered. Preliminary calculations showed that the value of Polanyi parameter is very close to 0.5, a typical value for a large number of heterogeneous catalytic reactions [23], therefore this value was fixed. Direct experimental data for Gibbs adsorption energy for sugars on different type of Ru sites (low and high coordinated) as

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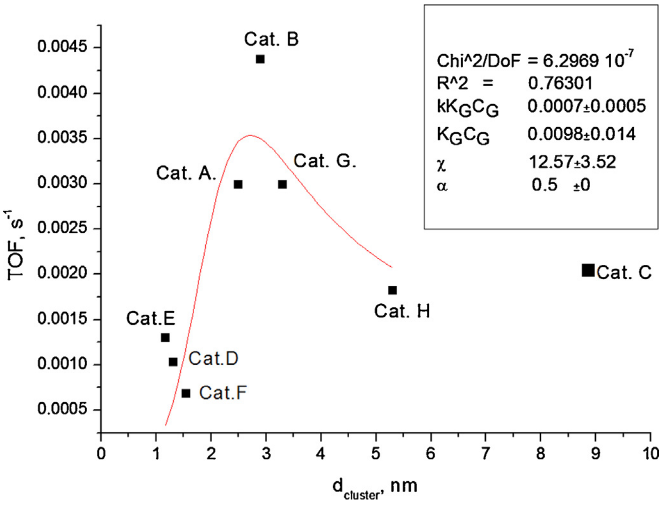

Fig. 9. Dependence of initial glucose conversion rates on the particle size of ruthenium.

well as theoretical calculations are not easily available in the literature, therefore not allowing verification of the difference in the Gibbs energy of adsorption on edges and terraces for glucose, which according to Fig. 9 amounts to ca. 41 kJ/mole.

4. Conclusions

Hydrogenation of glucose was performed in semi-batch mode at 120 °C and 19 bar hydrogen pressure over several Ru/C catalysts with different metal dispersion.

Catalysts with ruthenium particle sizes between 1.2 and 10 nm were investigated. All catalysts were active in glucose hydrogenation to sorbitol. Selectivity to sorbitol was fairly high (87–96%) with all catalysts except the catalyst with 10 nm particles.

A clear maximum in the dependence of TOF on cluster size was found for ruthenium nanoparticles of 2.9 nm. A model was proposed which quantitatively described this behavior.

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