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Kinetics of the catalytic hydrogenation of D-lactose on a carbon supported ruthenium catalyst

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Abstract

Catalytic hydrogenation of D-lactose to lactitol over various supported ruthenium catalysts was studied in a semi-batch slurry autoclave (300 ml, Parr Co.). 5% Ru/C (Johnson Matthey) had the best activity and gave the highest lactitol yield of the studied catalysts. Kinetic experiments of hydrogenation of aqueous D-lactose (1.31 mol/l) solutions on 5% Ru/C were performed at 40–60 bar hydrogen and 110–130 °C. The main hydrogenation product was lactitol, the selectivity varied between 96.5 and 98.5%, while small amounts of lactulose, lactulitol, sorbitol, galactitol and lactobionic acid were detected as by-products. The selectivity improved, as the hydrogen pressure increased and the reaction temperature decreased within the experimental range.

The kinetic data were modelled by Langmuir–Hinshelwood–Hougen–Watson (LHHW) rate expressions, assuming surface reaction steps being rate determining. Non-competitive adsorption of molecular hydrogen and lactose on the catalyst surface was assumed. The kinetic model was fitted to the experimental data by a combined Simplex–Levenberg–Marquardt method. The model predicted the experimental concentrations of lactose and lactitol very well. A reasonable good description of the by-products was obtained.

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Keywords: Lactose; Lactitol; Ruthenium; Hydrogenation; Kinetics

1. Introduction

Lactose, a milk sugar, is a reducing disaccharide consisting of glucose and galactose moieties. In aqueous solution at 20 °C, lactose coexists according to proton NMR analysis in two anomeric forms: 62.7% as β-lactose and 37.3% α-lactose [1]. The lactose contents of milks originating from different mammals vary between 0 and 9%, for instance, cow milk contains about 4.9% and human milk about 6.7% lactose [2]. The estimated annual worldwide availability of lactose as a byproduct from cheese manufacture is several million tons [2,3]. However, only about 400 000 t/a lactose is processed further from cheese whey [4]. Non-processed whey is an environmental problem due to its high biochemical and chemical oxygen demand [3]. A relatively low solubility of lactose in most solvents limits its use in many applications. Another restricting factor is the inability of lactose intolerant people, with a low level of lactase enzyme in the body, to digest milk sugar [2]. Therefore, development of value-added products from waste generated during cheese manufacturing processes is highly welcomed. Lactitol (by hydrogenation), lactulose (by isomerisation) and lactobionic acid (by oxidation) are the industrially most important lactose derivatives [5–8]. Moreover, the hydrolysis products of D-lactose, D-galactose and D-glucose, can be used as valuable raw materials by pharmaceutical industry [9,10].

Lactitol is a sugar alcohol, derived by reduction of the glucose part of the disaccharide, lactose. The lactose hydrogenation scheme in aqueous environment is displayed in Fig. 1. Lactitol is suitable for development of sugar-free, reduced calorie and low glycaemic index products, showing e.g. non-cariogenic and prebiotic properties. Lactitol is metabolised independently of insulin and as such it is suitable for diabetic diet. Lactitol can successfully replace sucrose in most applications due to many similar physical properties. Lactitol is a widely used ingredient

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Nomenclature

c	concentration (mol/dm^3)
E_a	activation energy (kJ/mol)
k	rate constant, (mol/s g_{CAT})
K	equilibrium constant
m_{CAT}	catalyst mass (g)
n	molar amount (mol)
p	pressure (bar)
r	reaction rate
R	gas constant (8.3143 J/mol K)
t	time (min)
T	temperature (K)
$\bar{T}$	average temperature (K)
V	volume
X	conversion
Greek letters	
ρ_B	catalyst bulk density (kg/dm^3)
ν	stoichiometric coefficient
Subscripts and superscripts	
i, j	reaction index
L	lactose
LB	lactobionic acid

for sugar-free chocolate, baked goods and ice cream applications [11–13].

Sugar alcohols, such as lactitol, xylitol and sorbitol, are industrially commonly prepared by catalytic hydrogenation of corresponding sugar aldehydes over sponge nickel and Ru/C catalysts [14–26,3]. Kinetics of D-glucose and D-xylose hydrogenation has been reported in several publications [19–24]. Literature about glucose hydrogenation kinetics is nicely summarized by Crezee in the introduction part of reference [20]. Only few studies about D-lactose hydrogenation have been published so far [1,3,25,26]. In reference [1], Table 2 summarized the catalyst screening results, showing Ru/C being the most active and selective catalyst for D-lactose hydrogenation to lactitol. In other publications, only sponge nickel catalysts have been used for D-lactose hydrogenation. Here we present experimental D-lactose hydrogenation data over Ru/C catalyst under industrially relevant reaction conditions [35] and kinetic modelling.

2. Experimental

2.1. Experimental setup

The D-lactose (40 wt% in water) hydrogenation experiments were carried out batchwise in a three-phase laboratory scale reactor (Parr Co.) operating at 40–60 bar and between 110 and 130 °C. The reactor was equipped with a heating jacket, a cooling coil, a filter (0.5 μm metal sinter) in a sampling line and a bubbling chamber (for removing dissolved air from the liquid phase prior to the hydrogenation experiments). The effective liquid volume of the reactor was about 125 ml (total volume 300 ml) and it was equipped with a hollow shaft concave blade impeller to ensure efficient mixing and gas dispersion into the liquid phase. The impeller rate was fixed at 1800 rpm in all of the kinetic experiments to ensure operation at the kinetically controlled regime [26]. A Parr 4843 controller was used for the temperature control and for monitoring the impeller speed and the reactor pressure. The temperature and pressure profiles were stored on a computer. Lactose solutions were prepared by dissolving D-lactose monohydrate (Valio, purity >99.5% of dry substance and dry substance content 95%) in deionized water. Too high lactose dissolution temperatures were avoided to suppress lactose hydrolysis prior to the hydrogenation. The amount of 5% Ru/C (Johnson Matthey) varied between 1.5 and 2.5 wt% (dry weight) of the lactose weight throughout the kinetic hydrogenation series. Catalyst screening experiments were performed at 120 °C and 50 bar hydrogen pressure with identical catalyst amount in each experiment. No pH buffer was used at lactose hydrogenation experiments.

Prior to the first hydrogenation batches, the supported ruthenium catalysts were reduced in the autoclave under hydrogen flow at 200 °C for 2 h (10 bar H_2, heating/cooling rate 5 °C/min). As the catalyst had been reduced, a lactose solution saturated with hydrogen was fed into the reactor rapidly and the hydrogen pressure and reactor temperature were immediately adjusted to the experimental conditions. Simultaneously, the impeller was switched on. This moment was considered as the initial starting point of the experiment. No notable lactose conversion was observed before the impeller was switched on.

2.2. Analysis and catalyst characterization

The reactor contents were analysed off-line with an HPLC equipped with a Biorad Aminex HPX-87C carbohydrate column. 1.2 mM $CaSO_4$ in deionized water was used as a mobile phase, since calcium ions improve the resolution of lactobionic acid [27]. A sample for pH measurement was withdrawn simultaneously as the HPLC sample was taken. An additional sample was withdrawn at the end of the hydrogenation batch to measure the amount of leached metals in the sugar solution. The dissolved metals were analysed by Direct Current Plasma (DCP) technique. The states of fresh and recycled sponge nickel catalysts were investigated by means of several catalyst characterization techniques (nitrogen adsorption BET, XPS surface analysis, SEM-EDXA, hydrogen TPD and particle size analysis) to reveal the underlying phenomena causing catalyst deactivation.

3. Catalyst screening results

The performances of several supported powdered ruthenium catalysts, commercial ones and synthesized at universities, for the hydrogenation of lactose to lactitol in aqueous solutions (1.31 mol/l), were studied in the semi-batch reactor. The catalyst screening experiments were performed at 120 °C and 50 bar hydrogen pressure. The catalyst amount was 8.96 g/l in each hydrogenation experiment, while the ruthenium loading varied between 3 and 5%. Following catalysts were prepared and

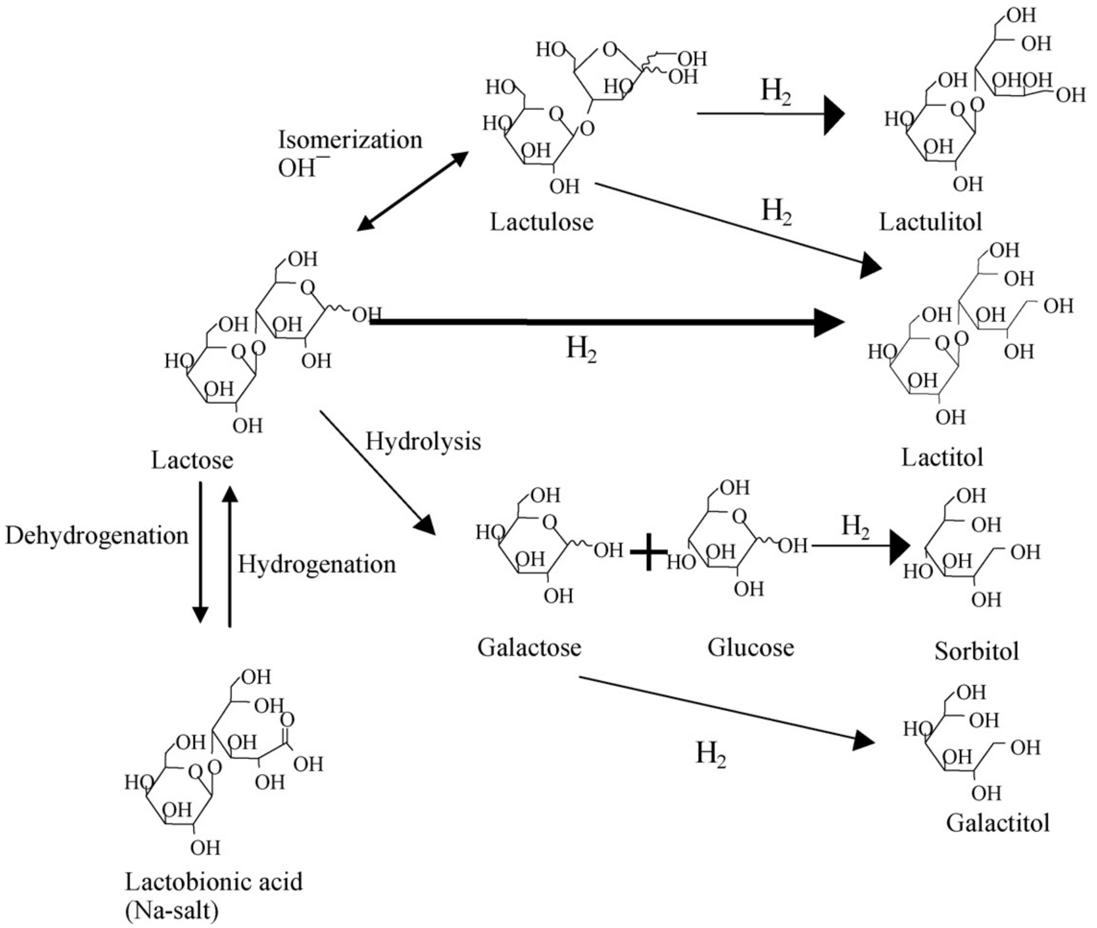

Fig. 1. The hydrogenation scheme of aqueous lactose solution.

tested: 5% Ru/C (Johnson Matthey), 5% Ru/Al_2O_3 (Fluka), 5% Ru/silica (synthesized at our laboratory by impregnation method from $H_{24}Cl_6N_{14}O_2Ru_3{\cdot}H_2O$), 5% Ru/$TiO_2$ (synthesized at our laboratory by impregnation method from $Ru(C_5H_7O_2)_3$), 5% Ru/MgO (synthesized at our laboratory) and 3% Ru/HPS (Ru on crosslinked polystyrene synthesized at Tver university). The commercial Ru/C catalyst showed clearly the best performance of these catalysts (Fig. 2). Some support materials, such as MgO and TiO_2 have a relatively low surface area, which probably affected the hydrogenation results on these materials. Hydrogenations on ruthenium supported on MgO, silica, alumina and TiO_2 led to clearly increased lactulose and to some extent lactobionic acid formation, which most probably accelerated catalyst deactivation too. The crosslinked polystyrene is a relatively acidic support material, which enhanced lactose hydrolysis, increasing thus galactitol and sorbitol formation. Previously, good lactose hydrogenation results have been obtained even with sponge nickel catalysts [26]. Related to the amount of active metal on the catalyst, ruthenium on carbon gives a substantially higher reaction rate compared to sponge nickel catalyst (Fig. 3). However, lactitol selectivities obtained both over Ru/C and sponge nickel catalysts are at equally high level (Fig. 4).

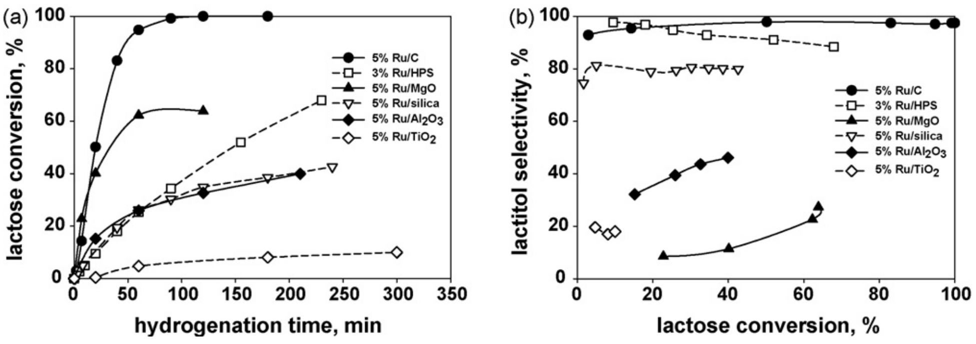

Fig. 2. Lactose (1.31 mol/l) conversion (a) and lactitol selectivity (b) over various supported ruthenium catalysts. $T = 120\,^{\circ}C$, $p = 50$ bar H_2 and catalyst amount 8.96 g/l in each experiment.

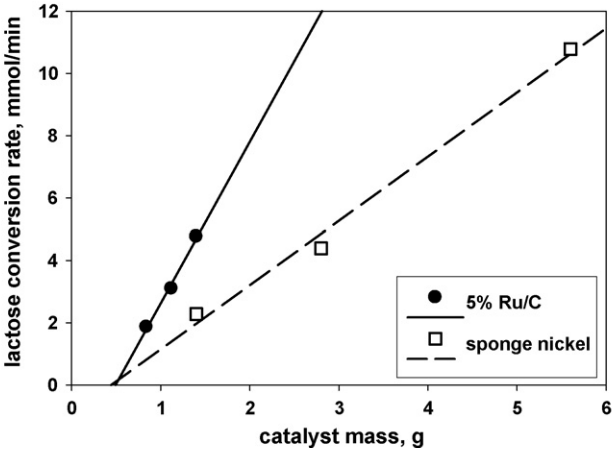

Fig. 3. The influence of catalyst amount on lactose (1.31 mol/l) conversion at 120 °C and 50 bar H_2 over 5% Ru/C and Mo-promoted sponge nickel catalysts.

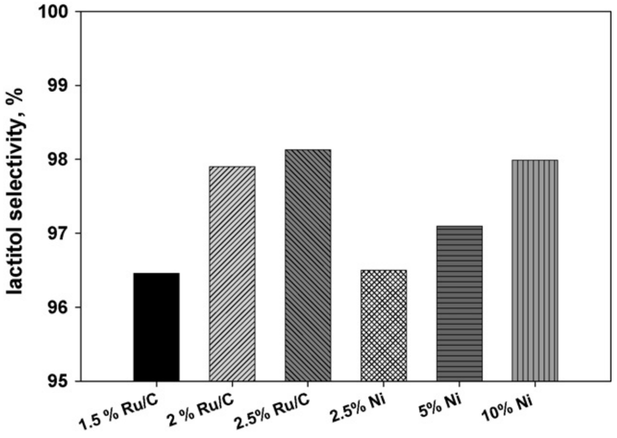

Fig. 4. The influence of catalyst amount on lactitol selectivity at 100% lactose conversion over 5% Ru/C and sponge nickel catalyst. Hydrogenation of 40 wt% aqueous lactose solution at 120 °C and 50 bar.

Systematic kinetic experiments were carried out with the commercial Ru/C catalyst.

4. Hydrogenation results over ruthenium on carbon

The influence of catalyst loading was evaluated by varying the catalyst-to-lactose ratio between 1.5 and 2.5 wt% in lactose hydrogenation experiments at 120 °C and 50 bar. As expected, higher hydrogenation rates were obtained with increased catalyst loadings (Fig. 3). The lactitol selectivities at 100% lactose conversion level were to some extent higher as the catalyst loadings were increased, the selectivity varying between 96.5 and 98.1% within the experimental range (Fig. 4).

The influence of the catalyst amount on the by-products formation is displayed in Fig. 5. There was a clear difference in the by-product distribution at altered catalyst amounts due to pH and mass transfer (g/l and l/s) effects. Lactobionic acid is formed from lactose under “hydrogen-poor” conditions on the catalyst surface, which will result as D-lactose dehydrogenation reaction involving hydrogen transfer from D-lactose. Hydrogen mass-transfer limited conditions (inefficient mixing, low hydrogen pressure or high hydrogen consumption due to high catalyst loading, pH and reaction temperature) enhance the formation of lactobionic acid. Of all the by-products formed, only lactobionic acid has an inhibiting effect on the lactose conversion and deactivates the catalyst by strongly adsorbing on active surface sites [26]. However, Ru/C catalyst is able to hydrogenate the lactobionic acid formed further to lactose and lactitol at a later stage of reaction (Fig. 5). Thus, Ru/C is not as prone to deactivation as sponge nickel catalyst [28]. Acidity and low reaction rate increase lactose and lactitol hydrolysis and thus, galactitol and sorbitol formation. A high pH value of the solution and hydrogen-poor conditions favour lactose isomerisation leading to increased lactulose and lactulitol formation. The hydrogen concentration in the liquid phase plays a crucially important role for the hydrogenations: in the case of external mass transfer of hydrogen, the isomerisation, hydrolysis and dehydrogenation reactions, which do not require any hydrogen, are favoured. Moreover, the concentration front moves towards the centre of catalyst particles, as the outer layer of the particle deactivates [29]. As the reaction progresses to high conversions, the role of diffusion resistance diminishes, because all of the reaction rates become lower.

From the experiments carried out at the temperature range at 383–403 K and at pressures 40–60 bar, it was found that the apparent activation energy for lactose hydrogenation over Ru/C was 54–73 kJ/mol (see the Arrhenius graph, Fig. 6). Thus the estimated activation energies were much larger than the activation energy of diffusion in liquids (12–21 kJ/mol) [22], thus indicating that the experiments were performed under kinetic

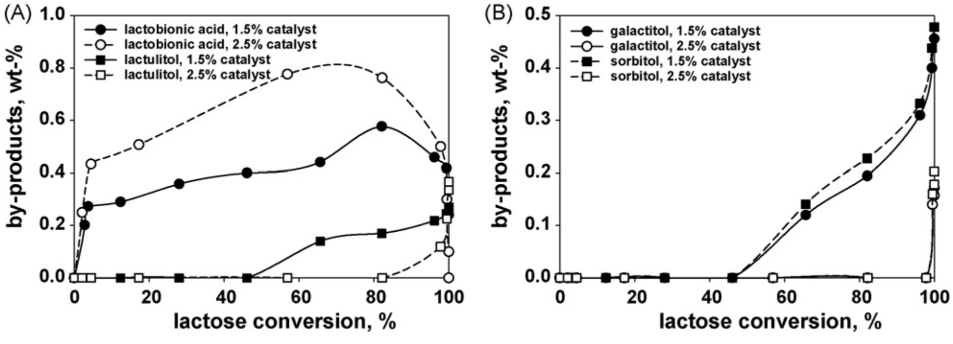

Fig. 5. The influence of catalyst amount of Ru/C on by-products formation at 120 °C and 50 bar H_2. (A) Lactobionic acid and lactulitol. (B) Galactitol and sorbitol.

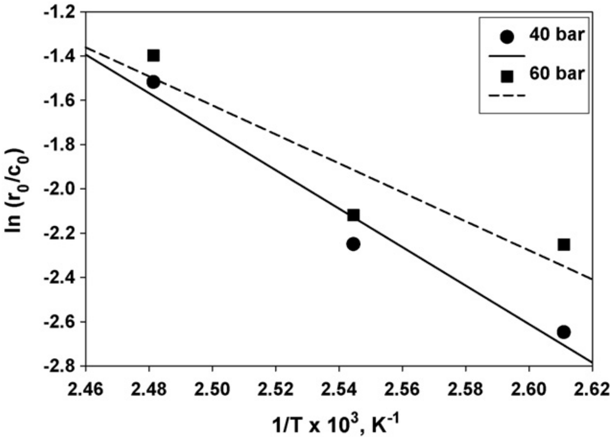

Fig. 6. Arrhenius plots of the initial lactose (40 wt% in water) hydrogenation rates carried out at 40 bar ($E_a = 72.3$ kJ/mol) and 60 bar (54.5 kJ/mol) and at the temperature range 383–403 K.

control. The effect of the reaction temperature on the lactose hydrogenation with 8.96 g/l Ru/C catalyst was clear. The increased hydrogenation temperature clearly improved the reaction rate at the experiments carried out between 110 and 130 °C (Fig. 7a). Elevated reaction temperatures increased to some extent the formation of the by-products, thus impairing the product selectivity (Fig. 7b). An increased hydrogen pressure had a positive effect on the reaction rate and lactitol selectivity, especially at lower temperatures. Performing experiments at clearly lower hydrogen pressure range, as demonstrated earlier in lactose hydrogenations on sponge nickel [26], would presumably have illustrated the crucial importance of hydrogen more clearly.

5. Modelling results

On the mechanistic level, rate equations can be based on the concepts of adsorption, surface reaction and desorption. It has previously been proposed by Mikkola et al. [23] that sugar hydrogenations follow a competitive adsorption model, where adsorbed atomic hydrogen is added pairwise to adsorbed organics. However, because of the large size difference between sugar molecules and hydrogen, it is, however, reasonable to assume that full competition in adsorption do not take place. Consequently, a semi-competitive adsorption model has been proposed in literature [30], but it is more difficult to determine the parameters of that model. Moreover, one can assume hydrogen being active either in molecular (H_2**) or in dissociative (H*) form. Eqs. (1) and (2) show the derived rate equations for non-competitive (Eq. (1)) and competitive models (Eq. (2))

$$r_j = \frac{k_j c_A p_{H_2}^{nH_2}}{(1 + K_{H_2} p_{H_2}^{nH_2})(1 + K_A c_A + K_B c_B)} \qquad (1)$$

$$r_j = \frac{k_j c_A p_{H_2}^{nH_2}}{(1 + K_{H_2} p_{H_2}^{nH_2} + K_A c_A + K_B c_B)^2} \qquad (2)$$

where $nH_2 = 1/\alpha$ ($\alpha = 1$ in case of molecular hydrogen and $\alpha = 2$ in case of dissociative hydrogen adsorption), and A and B denote organic components.

Since hydrogen molecules are much smaller than lactose molecules, interstitial sites between adsorbed lactose molecules are assumed to remain accessible for hydrogen adsorption. Thus, the adsorption behaviour is shifted towards a non-competitive one.

Based on preliminary kinetic analysis, some simplifications can be made. The amount of by-products in the liquid phase and thus also on the catalyst surface is minor and the main reaction turned out to be of first order with respect to lactose (this was proved by logarithmic plots). In addition, it is known that the adsorption affinity of sugar alcohols is much less than that of sugars. Furthermore, the product desorption step was excluded and the adsorption constants K_L and K_H were presumed to be independent of temperature. The rate constants (k_j) follow the law of Arrhenius (Eq. (3)),

$$k_j = k_{0,j} e^{-E_{a_j}/R(1/T - 1/\bar{T})} \qquad (3)$$

where $\bar{T}$ is the average temperature of the experiments. The final set of rate equations for a simplified reaction scheme (Fig. 8) became:

$$r_1 = \frac{(k_1 c_L p_{H_2})}{(1 + K_{H_2} p_{H_2})} \qquad (4)$$

$$r_2 = \frac{(k_2 c_L p_{H_2})}{(1 + K_{H_2} p_{H_2})} \qquad (5)$$

$$r_3 = \frac{(k_3 c_L p_{H_2})}{(1 + K_{H_2} p_{H_2})} \qquad (6)$$

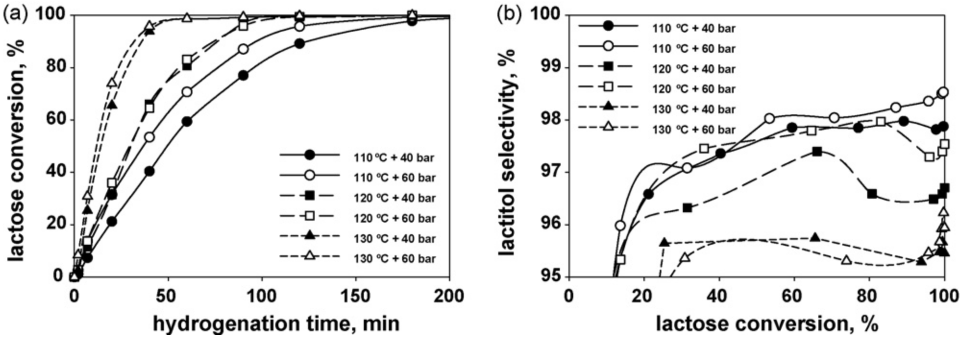

Fig. 7. The influence of hydrogenation temperature and pressure on (a) lactose conversion and (b) lactitol selectivity in the hydrogenation of 40 wt% aqueous solution of lactose on 8.96 g/l 5% Ru/C catalyst.

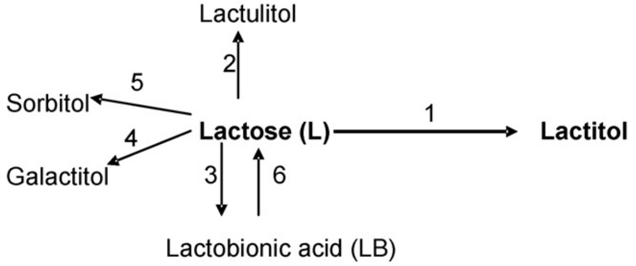

Fig. 8. A simplified lactose hydrogenation scheme used in modeling.

$$r_4 = \frac{(k_4 c_{\mathrm{L}} p_{\mathrm{H}_2})}{(1 + K_{\mathrm{H}_2} p_{\mathrm{H}_2})} \tag{7}$$

$$r_5 = \frac{(k_5 c_{\mathrm{L}} p_{\mathrm{H}_2})}{(1 + K_{\mathrm{H}_2} p_{\mathrm{H}_2})} \tag{8}$$

$$r_6 = \frac{(k_6 c_{\mathrm{LB}} p_{\mathrm{H}_2})}{(1 + K_{\mathrm{H}_2} p_{\mathrm{H}_2})} \tag{9}$$

The rate equations for hydrolysis reactions r_4 and r_5 are equal ($k_4 = k_5$). The above derived rate equations were further used in following mass balance equations for the organic components,

$$\frac{\mathrm{d}c_i}{\mathrm{d}t} = \sum \nu_{ij} r_j \rho_{\mathrm{B}}, \quad \text{where} \quad \rho_{\mathrm{B}} = \frac{m_{\mathrm{cat}}}{V_{\mathrm{L}}} \tag{10}$$

The catalyst bulk density was assumed constant during the experiments, since the amount of liquid withdrawn through sampling was negligible compared to the total liquid volume.

The fit of the experimental data to the kinetic model was carried out by Modest software [31] by using a combined Simplex-Levenberg-Marquardt method. The following objective function was used in data fitting:

$$Q = \sum (c_{i,\mathrm{exp}} - c_{i,\mathrm{calc}})^2 w_i \tag{11}$$

where the weight factors (w_i) were selected as follows: $w = 1$ for lactose and lactitol and $w = 5$ for by-products. Using higher weight factors for low-concentration components improved the estimation of them. The parameter estimation was performed for all experiments at different temperatures and pressures together.

Table 1
The results of parameter estimation

Parameter	Value	Standard deviation (%)
E_a1 (J/mol)	0.770E + 05	1.5
E_a2	0.178E + 06	0.1
E_a3	0.938E + 04	0.5
E_a4, Ea5	–	–
E_a6	0.664E + 05	30.4
k_{H_2} (l/mol)	0.297E − 01	16.1
$k1$ (mol/s g_{CAT})	0.233E − 03	9.7
$k2$	0.109E − 05	42.6
$k3$	0.158E − 05	40.7
$k4$, $k5$	0.193E − 05	15.4
$k6$	0.439E − 05	315.7

$T_{\mathrm{mean}} = 120\,^{\circ}\mathrm{C}$.

The results of parameter estimation are summarized in Table 1. As revealed by the table, the parameters are rather well identified. The parameters of the main reaction are well identified, the parameter standard deviations being below 10%. The parameters of the side reactions are not as accurately identified, but it should be kept in mind, that the concentrations of the by-products were very low, less than 0.5 wt%, while the concentrations of the main products were maximally 40 wt%. Fig. 9 illustrates that the proposed model nicely describes the behaviour of the system.

6. Catalyst deactivation and characterization

Catalyst deactivation was severe during consecutive lactose hydrogenation batches. However, deactivation over sponge nickel took place faster than over Ru/C [28]. Ruthenium leaching determined at the end of different hydrogenation batches, both in kinetic experiments and deactivation series, remained quite constant (around 13 ppm). The specific surface areas, pore volumes and pore size distributions of fresh and recycled catalyst samples were determined by nitrogen physisorption (Carlo Erba Sorptomatic 1900). In five lactose hydrogenation batches, recycled Ru/C catalyst had about 23% lower specific surface area and 16% decreased pore volume compared to the fresh one (Table 2).

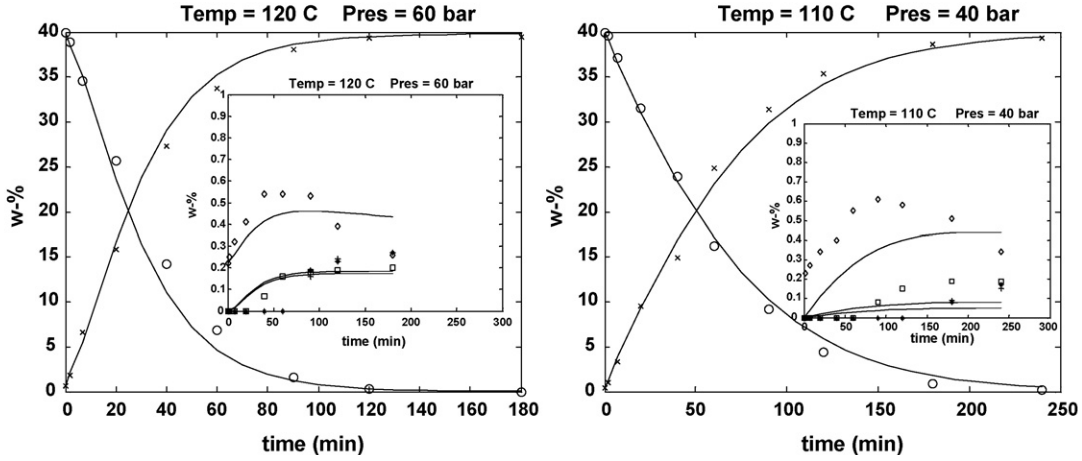

Fig. 9. Model fit to some lactose hydrogenation experiments: lactose (◯), lactitol (×), lactobionic acid (◇), lactulitol (□), galactitol (+) and sorbitol (*).

Table 2
The specific surface area and pore volume of the Ru/C catalysts

Sample	Fresh	Recycled
Specific surface area (m^2/g catalyst)	806.8	621.8
Specific pore volume (ml/g catalyst)	0.7784	0.6569

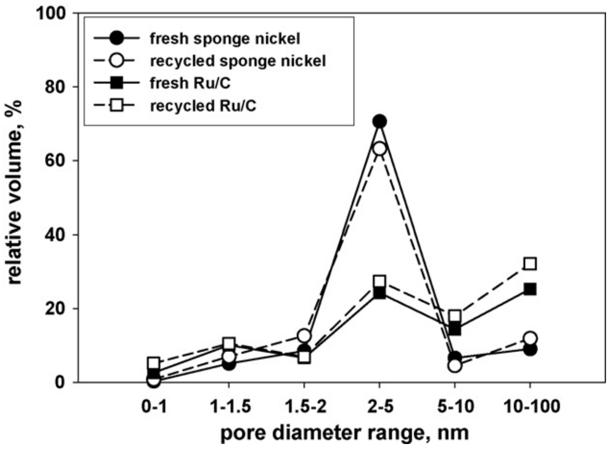

Fig. 10. Pore size distribution of fresh and for consecutive lactose hydrogenation batches used sponge nickel (three batches) and Ru/C (five batches) catalysts.

Table 3
XPS-analysis of Ru/C catalyst surfaces

Sample	Fresh	Reduced	Recycled
Ru (wt%)	8.0	9.3	4.6
C (wt%)	73.2	74.0	77.3
O (wt%)	18.8	16.7	18.1
Ru $2p_{3/2}$ peak interpretation, relative area			
RuO (%)	0	77	72
RuO_2 (%)	63	0	0
RuO_3 (%)	23	23	18
RuO_4 (%)	14	0	10
Theoretical surface composition	$Ru_1O_{14.8}C_{76.8}$	$Ru_1O_{11.4}C_{67.2}$	$Ru_1O_{25.2}C_{143}$

The comparison of pore size distributions of fresh and recycled sponge nickel and Ru/C catalysts reveals that Ru/C has relatively more large pores (5–100 nm) and sponge nickel pores are mainly in the range of 2–5 nm (Fig. 10). Smaller catalyst pores around 2 nm may get easily blocked by lactose molecule and the hydrogenation products of it, especially by strongly adsorbing lactobionic acid, therefore offering a feasible explanation for faster deactivation of the sponge nickel catalysts.

SEM-EDXA analysis (analysis area ∼10 μm × 10 μm) revealed that ruthenium was not homogeneously distributed on carbon support (Fig. 11a). Fig. 11b displays the surface morphology of the reduced catalyst. According to SEM-EDXA analysis, reduced Ru/C catalyst contained 8.3 wt% and recycled catalyst 6.1 wt% ruthenium. The catalyst particle size distributions were measured by Malvern 2600. The median particle size of the fresh catalyst was 20.8 μm, 10% of particles being larger than 45.5 μm and 10% less than 5.1 μm. According to particle size analysis, the amount of fines decreased in consecutive lactose hydrogenation experiments and thus, the median particle size increased. Most probably some catalyst fines were lost in repeated hydrogenations.

The chemical states of fresh, reduced and recycled catalyst surfaces were analysed by X-ray photoelectron spectroscopy (Perkin-Elmer 5400 ESCA system). Monochromatised Al Kα X-ray source was used with sensitivity factors of 1.349, 0.296 and 0.711 for Ru $2p_{3/2}$, C 1s and O 1s, respectively [32]. A flood gun was used to prevent sample charging under X-ray bombardment and no charging of the sample was observed. Carbon 1s photoelectron line was observed at 285.0 ±0.1 eV. Spectral background due to inelastically scattered electron was removed using the method by Shirley [33]. Fresh catalyst was in the form of dry powder and mounted on a two-sided tape for the XPS analysis. Treated catalysts were stored in water or ethanol solvent, mounted on a cup-shaped sample holder for the XPS analysis, and dried in vacuum. As RuO_2 is heated in oxygen, e.g. during catalyst calcination, formation of RuO_3 and RuO_4 takes place [34]. For this reason the Ru $2p_{3/2}$ line was used instead for quantitative analysis and analysis of the chemical state. A summary of XPS-analysis is provided in Table 3.

The reduced Ru/C catalysts‘ability to adsorb hydrogen was determined by hydrogen TPD (AutoChem 2910 instrument, Micromeritics Instrument Corporation). First catalyst sample was reduced with a gas mixture (50 ml/min H_2 and 10 ml/min Ar) at 200 °C (heating rate 5 °C/min) for two hours. After completed reduction, the temperature was cooled down to a

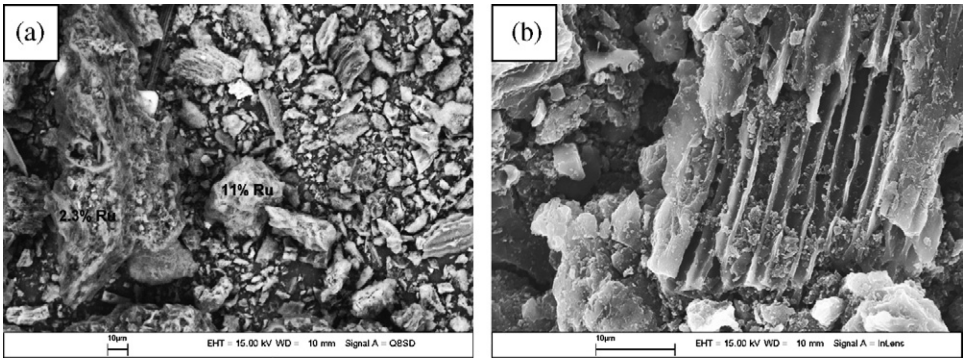

Fig. 11. Scanning electron microscopy (SEM-EDXA) image of (a) fresh (×500) and (b) reduced Ru/C catalysts (×2000).

typical lactose hydrogenation temperature 120 °C. Hydrogen adsorption was continued at this temperature with the same gas mixture for 50 min. Before hydrogen TPD, physisorbed hydrogen was removed with an argon flow (15 ml/min for 45 min). The hydrogen desorption temperature was increased 10 °C/min from adsorption temperature until 600 °C, where the desorption was continued for 40 min. According to the measurement, the reduced catalyst was able to adsorb 0.290 mmol H_2/g catalyst at 120 °C.

7. Conclusions

The kinetics of lactose hydrogenation to lactitol on Ru/C catalyst in aqueous solutions was studied. High lactitol yields (>98%) can be achieved in relatively short reaction times over Ru/C catalysts. Small amounts of lactobionic acid, lactulose, lactulitol, galactitol and sorbitol were detected as by-products. The selectivity values improved slightly, as the hydrogen pressure increased and the reaction temperature decreased at the experimental range. Hydrogen mass-transfer limited conditions (inefficient mixing, low hydrogen pressure or high hydrogen consumption due to elevated catalyst loading, pH and reaction temperature) enhance the formation of lactobionic acid, lactulose and lactulitol. High temperature, acidity and slow reaction rate increase lactose hydrolysis, promoting galactitol and sorbitol formation.

Ru/C catalyst deactivation was severe, but not as fast as sponge nickel deactivation, during consecutive lactose hydrogenation batches [28]. In five consecutive lactose hydrogenation batches, recycled Ru/C catalyst had about 23% lower specific surface area and 16% decreased pore volume compared to the fresh one (Table 2). As a by-product formed lactobionic acid accelerates catalyst deactivation [26]. Ru/C catalyst was able to hydrogenate the lactobionic acid formed further to lactose and lactitol at a later stage of reaction. Thus, Ru/C is not as prone to deactivation as sponge nickel catalyst.

The kinetic data were modelled, based on a Langmuir–Hinshelwood model. Based on the preliminary kinetic analysis, some simplifications were made. The amount of by-products in the liquid phase and thus also on the catalyst surface were minor and the main reaction turned out to be of first order with respect to lactose. In addition, it is known that the adsorption affinity of sugar alcohols is much less than that of sugar aldehydes. Furthermore, the product desorption step was excluded and the adsorption constants K_L and K_H were presumed to be independent of temperature. The parameter estimation was performed for all experiments at different temperatures and pressures together. Parameter estimation results indicated that the main reaction, lactitol formation, can be described very well by the model and the side reactions reasonably well (Fig. 9).

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