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# Enhancing consecutive reactions during three phase hydrogenation with a semibatch liquid phase

Päivi Mäki-Arvela*, Arnaud Denecheau, Kasper Alho, Johan Wärnå, Kari Eränen, Tapio Salmi, Dmitry Yu. Murzin

*Process Chemistry Centre, Åbo Akademi University, FI-20500 Turku/Åbo, Finland*

## Abstract

Kinetics for citral hydrogenation was investigated over a $Ni/Al_2O_3$ catalyst both in semibatch and in batch mode with respect to the liquid phase. In the former case the liquid phase was pumped out from the reactor continuously, while the amount of catalyst was kept constant during the hydrogenation in the latter case. The idea with liquid phase drainage was to increase the catalyst bulk density with increasing reaction time. The effect of increasing catalyst bulk density on reaction kinetics and selectivity was investigated both qualitatively and quantitatively. The main parameters were hydrogen pressure (5–21 bar) and temperature (50–90 °C). The product selectivity, which should theoretically be independent on the changes in catalyst bulk density, varied with varying catalyst bulk density, especially at higher reaction temperatures due to catalyst deactivation. The simplified kinetic model with lumped kinetic and deactivation parameters was applied to the experimental data being able to explain results obtained under semibatch conditions with continuous liquid phase drainage out of the reactor.

*Keywords:* Hydrogenation; Consecutive reaction; Kinetic modeling; Semibatch reactor

## 1. Introduction

In complex heterogeneously catalyzed liquid phase reactions the desired products can be formed in consecutive steps. This is the case for example in the formation of citronellol as a secondary product in citral hydrogenation [1,2]. The rate of the second step can be significantly lower, thus investigation of reaction kinetics can represent substantial challenges. There are several methods to enhance the reaction rates and to produce higher yields of the desired products, i.e. utilization of higher temperatures and pressures or application of higher amounts of catalysts. Another method to enhance the reaction rates is to use temperature-programmed experiments, which has, however, a potential drawback, since they can lead to increased amount of side products. From the engineering point of view it might be beneficial to enhance the rates of secondary reactions giving the desired products, not by temperature increase, but by increasing the catalyst bulk density during the reaction.

It is important in the studies of the catalytic reactions to investigate intrinsic reaction kinetics in the region free from gas/liquid mass transfer, external and internal diffusion. This is achieved over small catalyst particles in conditions with efficient stirring, when initial hydrogenation rates are linearly dependent on the catalyst mass [3]. Interestingly it has been experimentally shown that selectivity to an intermediate product can be changed with increasing catalyst concentration even if the reaction rate increases linearly with the catalyst mass. This was the case for cinnamaldehyde hydrogenation over Pt-alloy catalysts in the kinetic regime, when the selectivity to cinnamyl alcohol increased or decreased depending on temperatures as a function of catalyst loading [4], the reason being in changes of reactant adsorption modes with different catalyst bulk densities. According to our knowledge there are almost no reports available in the literature describing quantitatively the effect of catalyst bulk density on reaction rates and product selectivities in three-phase hydrogenations.

In this work the main aim was to compare the effect of liquid phase drainage out of the reactor during three-phase hydrogenation of a model molecule, in this case citral, with a conventional case of a constant catalyst bulk density. The working hypothesis in this work by using increasing catalyst bulk density during the reaction was to increase the rates of the consecutive reactions and facilitate the determination of their rate constants in a more reliable way. On the other hand the product selectivities should

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* Corresponding author. Tel.: +358 2 2154424.
*E-mail address:* paivi.maki-arvela@abo.fi (P. Mäki-Arvela).

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**Nomenclature**

| | |
|---|---|
| $A$ | frequency factor ($\mathrm{l^2/(mol\,min\,g)}$) |
| $c$ | concentration (mol/l) |
| $E_a$ | activation energy (J/mol) |
| $i$ | product |
| $k$ | rate constant ($\mathrm{l^2/(mol\,min\,g)}$) |
| $K$ | adsorption constant (l/mol) |
| $m$ | mass (g) |
| $n$ | mole (mol) |
| $n'$ | molar flow (mol/min) |
| $p$ | pressure (bar) |
| $Q$ | object function $\mathrm{(mol/l)^2}$ |
| $r$ | generation rate (mol/(g min)) |
| $R$ | gas constant J/(mol K) |
| $R^2$ | degree of explanation (%) |
| $t$ | reaction time (min) |
| $T$ | temperature (°C, K) |
| $V$ | volume (l) |
| $\dot{V}$ | volumetric flow (l/min) |
| $x$ | mole fraction |

*Greek letters*

| | |
|---|---|
| $\rho$ | density (g/l) |
| $\upsilon$ | stoichiometric coefficient |

theoretically remain unaffected with the change in catalyst bulk density, when working in the kinetic regime. The selectivities reported above for cinnamaldehyde hydrogenation are regarded as an exception, since this substrate can adsorb in different ways on the catalyst surface. The first task was to identify, whether the kinetic data fulfill the working hypothesis, i.e. at first enhanced consecutive reaction rates and at second the unaffected selectivities in the presence and in the absence of liquid phase drainage should be achieved.

Three-phase hydrogenation is very demanding reaction, since catalyst deactivation can be very severe in the hydrogenation of α,β-unsaturated aldehydes, especially at higher temperatures [1]. Both catalyst deactivation and mass transfer limitations can change the product selectivities with increasing reaction times. In this work we will demonstrate the idea of working in three-phase hydrogenations with a semibatch liquid phase operation fulfilling the first working hypothesis. On the other hand the second criterion, i.e. the same product selectivities unaffected by the changes in catalyst bulk densities, were not easily achieved. In this work both mechanistic model and simplified model were derived, and the latter one was applied to a limited kinetic data set.

## 2. Experimental

### 2.1. Reactor set-up

Three-phase hydrogenation was performed in batch and in semibatch modes with respect to the liquid phase. When liquid phase was pumped out from the reactor, the catalyst bulk density increased with increasing reaction time. The catalyst mass was kept constant in all experiments (500 mg) and the stirring rate was 1500 rpm. The use of small catalyst particles and vigorous stirring facilitated the hydrogenation under kinetic regime [3,5]. In the experiments with increasing catalyst bulk density about 1 g/min liquid was pumped out and the initial liquid phase volume was 325 ml. The mass of the liquid phase, which was pumped out from the reactor, was continuously recorded and taken into account in the kinetic model.

### 2.2. Case study: citral hydrogenation

Citral (Alfa Aesar, 97%) hydrogenation kinetics was investigated in an autoclave in 2-pentanol (>98%, Merck 807501) as a solvent in the temperature and pressure range of 50–90 °C and 5–21 bar, respectively. The $Ni/Al_2O_3$ (20.2 wt.% Ni) catalyst with a mean particle size of 13.5 μm (sieved below 100 μm) was reduced prior to the experiment in situ at 270 °C for 90 min with flowing hydrogen (99.999%, AGA). The initial citral concentration and the initial liquid phase volume were 0.1 mol/l and 325 ml, respectively. The catalyst, used in this work, was characterized in our previous work [2] and the following properties were obtained: BET surface area 111 $m^2/g_{cat}$, dispersion $D = 15.7\%$. The liquid samples were analyzed with a gas chromatograph (Agilent Technologies 6890N) equipped with a capillary column (DB-1, length 30 m, internal diameter 0.25 mm, film thickness 0.50 μm). The following temperature program was used for analysis: 120 °C (1 min)–0.3 °C/min to 122 °C (1 min)–3 °C/min–125 °C (1 min)–0.2 °C/min–126 °C–20 °C/min–200 °C (15.63 min).

## 3. Semibatch reactor for complex three-phase reactions

Citral was used as a model molecule and the reaction scheme of its transformations is presented in Fig. 1. The effect of catalyst bulk density on the hydrogenation kinetics and on selectivity was investigated both qualitatively and quantitatively with kinetic modeling. The main parameters in this work were temperature, pressure and the operation mode, i.e. application of either liquid-phase drainage or constant catalyst bulk density. In some experiments, the kinetics was investigated by temperature-programmed technique. In complex three-phase hydrogenations, such as citral hydrogenation [6,7], the desired product can be formed as a secondary or tertiary product

$$A \rightarrow B \rightarrow C \rightarrow D \rightarrow \cdots \tag{1}$$

where A, B, C and D denote citral, citronellal, citronellol and 3,7-dimethyloctanol, respectively. Furthermore, small amounts

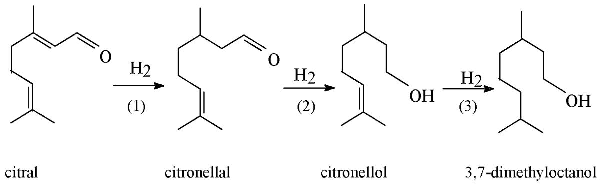

Fig. 1. Simplified reaction scheme for hydrogenation of citral on $Ni/Al_2O_3$.

of the desired product are formed within a short reaction time. In order to enhance the formation rate of consecutive products and to determine their rate constants in a more reliable way, a three-phase batch reactor was operated in a semibatch manner, i.e. liquid phase was continuously pumped out from the reactor, while the amount of catalyst was kept constant (see Section 2). The bulk density of the catalyst in the semibatch reactor changes as a function of time

$$\rho_{\mathrm{B}} = \frac{m_{\mathrm{cat}}}{V_{0\mathrm{L}} - \dot{V}_t} \tag{2}$$

where $\rho_{\mathrm{B}}$ is the catalyst bulk density, $m_{\mathrm{cat}}$ mass of catalyst, $V_{0\mathrm{L}}$ initial liquid phase volume, $\dot{V}$ liquid phase volumetric flow and $t$ time.

Rate constants can be determined by using a following mass balance for a semibatch reactor with a decreasing liquid phase volume

$$\frac{\mathrm{d}n_i}{\mathrm{d}t} = r_i m_{\mathrm{cat}} - \dot{n}_{i,\mathrm{out}} \tag{3}$$

where $n_i$ is the molar amount and $n_{i,\mathrm{out}}$ is the molar flow of component '$i$'. $r_i$ denotes the generation rate of '$i$'. Diffusion around the catalyst particle in the liquid film is negligible, when the catalyst particles are small and the reaction slow. The concentrations in the continuously pumped volume flows are constant in the reactor, i.e. $c_{i,\mathrm{out}} = c_i$ due to the extensive stirring.

Mass balance equation can be written as

$$\frac{\mathrm{d}n_i}{\mathrm{d}t} = r_i m_{\mathrm{cat}} - c_{i,\mathrm{out}}\dot{V}_{\mathrm{out}} \tag{4}$$

where '$i$' denotes a component. The amount of moles is $n_i = c_i V_{\mathrm{L}}$ where both $c_i$ and $V_{\mathrm{L}}$ will be changed with the reaction time. The mass balance is written as

$$\mathrm{d}\frac{(c_i V_{\mathrm{L}})}{t} = r_i m_{\mathrm{cat}} - c_{i,\mathrm{out}}\dot{V}_{\mathrm{out}} \tag{5}$$

$$\left(\frac{\mathrm{d}c_i}{\mathrm{d}t}\right) V_{\mathrm{L}} + \left(\frac{\mathrm{d}V_{\mathrm{L}}}{\mathrm{d}t}\right) c_i = r_i \Delta m_{\mathrm{cat}} - c_{i,\mathrm{out}}\dot{V}_{\mathrm{out}} \tag{6}$$

$$\frac{\mathrm{d}c_i}{\mathrm{d}t} = r_i \frac{m_{\mathrm{cat}}}{V_{\mathrm{L}}} - \frac{\mathrm{d}V_{\mathrm{L}}}{\mathrm{d}t}\frac{c_i}{V_{\mathrm{L}}} - \frac{c_{i,\mathrm{out}}\dot{V}_{\mathrm{out}}}{V_{\mathrm{L}}} \tag{7}$$

where $\mathrm{d}V_{\mathrm{L}}/\mathrm{d}t = -\dot{V}_{\mathrm{out}}$ and $c_{i,\mathrm{out}} = c_i$ and the mass balance is simplified to

$$\frac{\mathrm{d}c_i}{\mathrm{d}t} = r_i \frac{m_{\mathrm{cat}}}{V_{\mathrm{L}}} = \rho_{\mathrm{B}} r_i \tag{8}$$

where $\rho_{\mathrm{B}}$ is given by Eq. (2) and $r_i$ is determined by the stoichiometry, i.e. $r_i = \Sigma \nu_{ij} r_j$.

Since the catalyst bulk density ($\rho_{\mathrm{B}}$) varies with time, the obtained kinetic data can be normalized as follows. Separation of variables of Eq. (8) yields

$$\int_{c_{0i}}^{c_i} \frac{\mathrm{d}c_i}{r_i} \int_0^t \rho_{\mathrm{B}}\,\mathrm{d}t, \quad \rho_{\mathrm{B}} = \frac{\rho_0}{1 - t/\tau_0} \tag{9}$$

where $\rho_{0\mathrm{B}} = m_{\mathrm{cat}}/V_{0\mathrm{L}}$ and $\tau_0 = V_{0\mathrm{L}}/\dot{V}$ (see Eq. (2)). Integration of the right-hand side of Eq. (9) yields finally

$$\int_{c_{0i}}^{c_i} \frac{\mathrm{d}c_i}{r_i} = \rho_{0\mathrm{B}}\tau_0 \ln\left(1 - \frac{t}{\tau_0}\right)^{-1} \tag{10}$$

Eq. (10) suggests that concentration data plotted against $\rho_{0\mathrm{B}}\tau_0 \ln(1 - t/\tau_0)^{-1}$ should coincide, provided that data are obtained within kinetic regime and effects related to catalyst deactivation (e.g. irreversible adsorption of species, coking, sintering) are absent. For cases that no liquid drainage is applied the right-hand side of the Eq. (10) reduces to $\rho_{0\mathrm{B}}t$.

## 4. Qualitative kinetics

It follows clearly from Fig. 2, that when citral hydrogenation was carried out on $Ni/Al_2O_3$ catalyst in 2-pentanol at three different temperatures (50, 70 and 90 °C) at 10 bar hydrogen with and without liquid phase drainage, the kinetic data presented (Fig. 2) as a function of normalized abscissa do not coincide. In all the cases the time interval to reach a certain conversion level is much lower for the case of drainage.

In the current kinetic data the effect of film diffusion is absent, since the apparent activation energy with liquid phase drainage was 21 kJ/mol and zero order kinetics was achieved in respect to hydrogen above 10 bar. The possible reason for varying activities and selectivities in the absence and in the presence of liquid phase drainage is most probably catalyst deactivation. The latter was less prominent with higher catalysts bulk densities, indicating that the catalyst was less deactivated when the amount of reactant per gram nickel decreased. Analogous results have been previously obtained in the hydrogenation of β-sitosterol over supported Pd catalyst [9]. The catalyst deactivation in citral hydrogenation has been previously observed over Pt [7,8] and over Ru supported catalysts [10].

More recently a significant decrease in conversion [11] from 40 to 20% within 40 min time-on-stream was obtained in liquid phase citral hydrogenation in ethanol over a fixed bed of $Ni/SiO_2$ catalyst operating already at 25 °C, and 6.1 bar total pressure, clearly demonstrating significant deactivation.

In citral hydrogenation over $Pt/Al_2O_3$ the initial hydrogenation rates as a function of temperature did not follow Arrhenius law, but instead exhibited a maximum as a function of temperature [7]. The reason for catalyst deactivation is most probably blocking of the active sites due to decarbonylation of unsaturated alcohols.

Qualitatively somewhat unusual difference between kinetic data presented on Fig. 2 could be explained by the fact, that when a certain part of the liquid is pumped out of the reactor the catalyst to reactant concentration increases along with the fraction of sites, which are not irreversibly blocked presumably by formed CO. This leads to the situation, when the so-called effective catalyst mass, e.g. the amount of catalyst available for the reaction, is higher in the case of liquid drainage.

As the conversions are compared at time = 25 g/l min it turned out that with increased catalyst bulk density con-

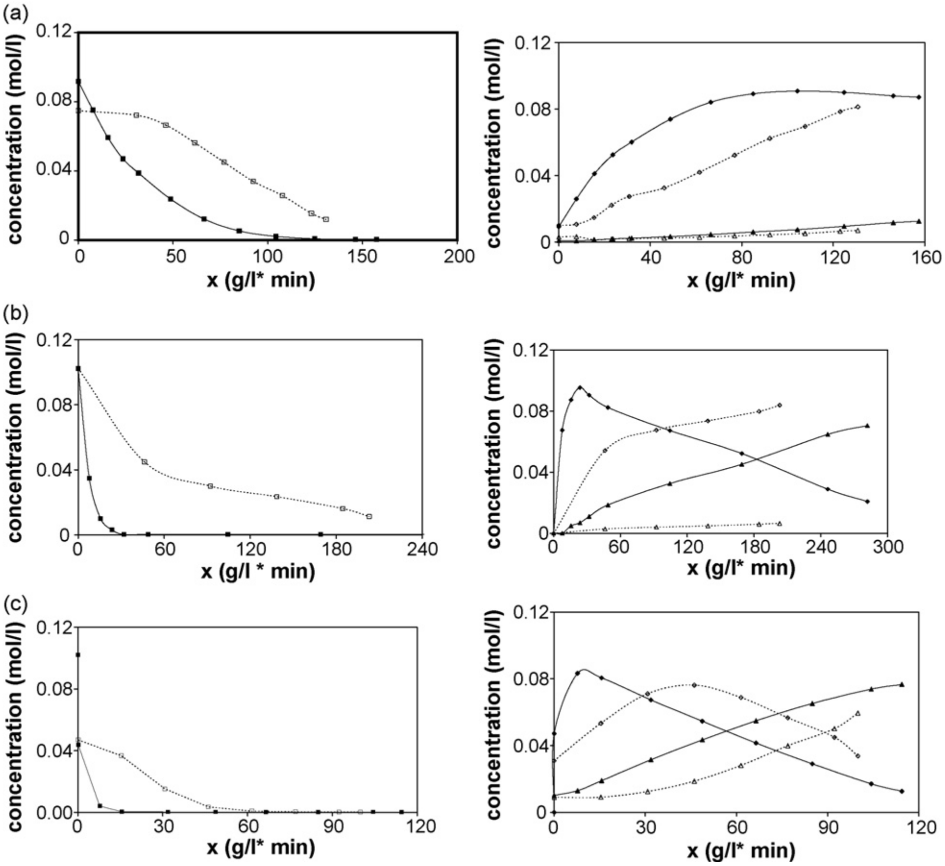

Fig. 2. Kinetics for citral (■) hydrogenation, formation of citronellal (♦) and citronellol (▲) with (solid symbol) and without liquid phase drainage (open symbol) in the hydrogenation of citral in 2-pentanol under 10 bar hydrogen at (a) 50 °C, (b) 70 °C and (c) 90 °C. The abscissa $x$ denotes without liquid drainage $x = \rho_{0B} t$ and with liquid drainage $x = \rho_{0B} \tau_0 \ln(1 - t/\tau_0)^{-1}$.

version increased 2.1-fold at 50 °C and 2.8-fold at 70 °C and at 90 °C complete conversion was achieved already at $\rho_{\mathrm{bulk}} \times \mathrm{time} = 25$ g/l min. The *cis*-to-*trans* isomer ratio as a function of $\rho_{\mathrm{bulk}} \times$ time decreased with increasing temperature indicating that *cis* citral reacted faster than *trans* citral at higher temperatures (Fig. 3).

Product selectivity to citronellal and citronellol are given in Fig. 4 for experiments with and without liquid phase drainage. Only traces of nerol and geraniol in citral hydrogenation over $Ni/Al_2O_3$ catalyst were formed opposite to $Pt/Al_2O_3$ catalyst [7,8]. Formation of isopulegol was not observed.

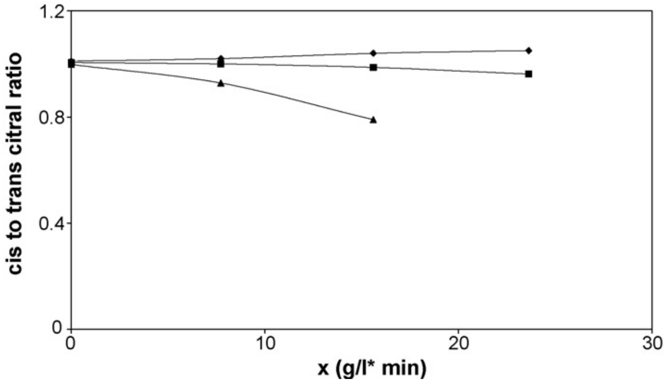

Fig. 3. *Cis*-to-*trans* citral ratio in citral hydrogenation with liquid phase drainage at hydrogen pressure of 10 bar and (♦) 50 °C, (■) 70 °C and (▲) 90 °C. The abscissa $x$ with liquid drainage denotes $x = \rho_{0B} \tau_0 \ln(1 - t/\tau_0)^{-1}$.

In principle the catalyst bulk density should not affect the product selectivities, if the experiments are performed under kinetic regime without interference of other processes, e.g. deactivation. In citral hydrogenation about the same selectivity was achieved at 50 °C and 10 bar with and without drainage, whereas at 70 and 90 °C the values were different. Especially at 70 °C the formed citronellal was not reacting further to citronellol and the selectivity to citronellal was nearly constant, about 93%. The reason for these results is the faster catalyst deactivation and additionally mass transfer limitations at higher temperatures.

The effect of liquid phase drainage was investigated at 70 °C at three different pressures (Table 1, Fig. 5). It turned out the

Table 1
Comparison between concentrations of different products at $\rho_{\mathrm{bulk}} \times \mathrm{time} =$ ,25 g/l min at different hydrogen pressures at 70 °C in citral hydrogenation under liquid phase drainage

| Pressure (bar) | $S_{\mathrm{CAL}}$ (%) | $S_{\mathrm{COL}}$ (%) | $S_{\mathrm{DMOL}}$ (%) | $S_{\mathrm{DNAL}}$ (%) |
|---|---|---|---|---|
| 5 | 77 | 22 | 1 | 1 |
| 10 | 37 | 57 | 4 | 2 |
| 21 | 30 | 55 | 8 | 5 |

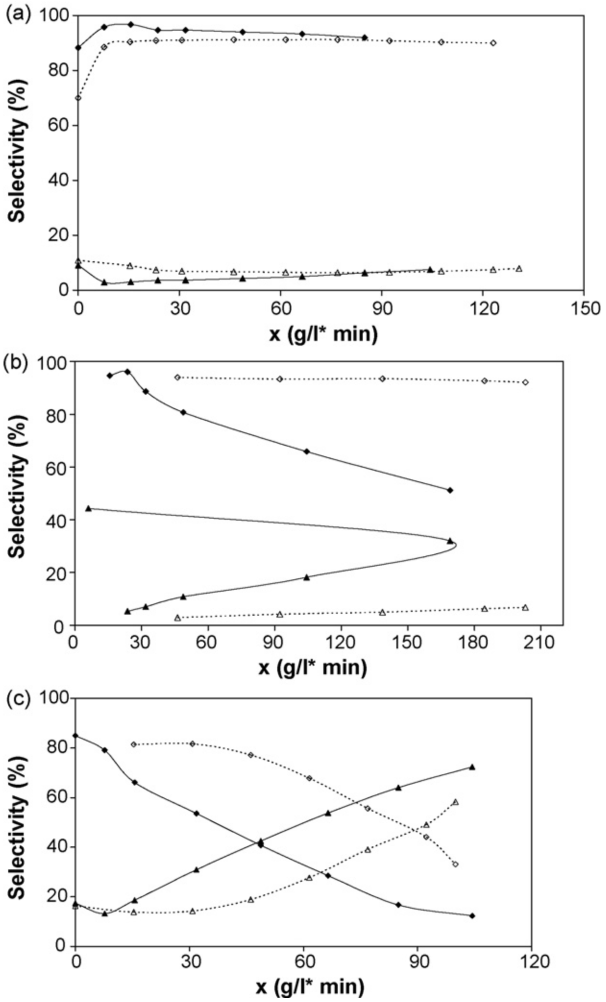

Fig. 4. Selectivity as a function of normalized abscissa $\rho_{\mathrm{bulk}} \times \mathrm{time}$ at (a) 50 °C, (b) 70 °C and (c) 90 °C. Symbols: solid line (with liquid drainage), dotted (without liquid drainage), (♦) citronellal and (▲) citronellol. The abscissa $x$ denotes without liquid drainage $x = \rho_{0B} t$ and with liquig drainage $x = \rho_{0B} \tau_0 \ln(1 - t/\tau_0)^{-1}$.

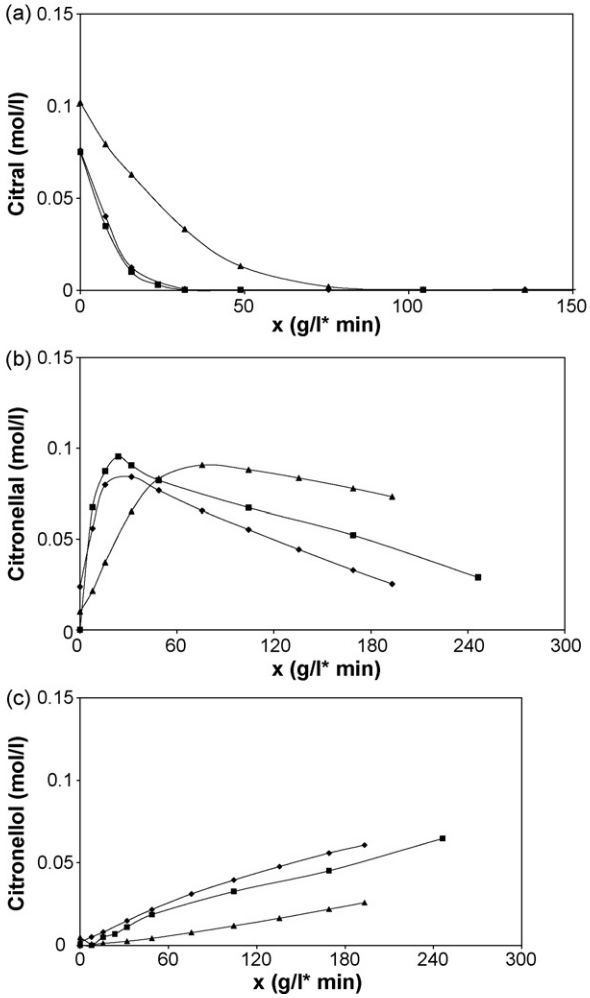

Fig. 5. Kinetics in (a) citral hydrogenation, (b) formation of citronellal and (c) citronellol at 70 °C at different hydrogen pressures (▲) 5 bar, (■) 10 bar and (♦) 21 bar with liquid phase drainage. The abscissa $x$ denotes with liquid drainage $x = \rho_{0B} \tau_0 \ln(1 - t/\tau_0)^{-1}$.

reaction order with respect to hydrogen was equal to unity at low pressures, below 10 bar, whereas above 10 bar it was zero.

The *cis*-to-*trans* citral ratio was close to one at all the three pressures and no systematic trend was observed. The concentration profiles as a function of coordinate, corresponding to the liquid drainage, for citronellal and citronellol given in Fig. 5 demonstrates that at higher pressures citronellal reacted further to citronellol and 3,7-dimethyloctanal followed by the formation of 3,7-dimethyloctanol (not shown). The initial selectivity to the products is given as well in Table 1 at a catalyst bulk density at $\rho_{\mathrm{bulk}} \times \mathrm{time} = 25$ g/l min. In the present work selectivity to citronellal at 10 bar and 70 °C in 2-pentanol with liquid phase drainage was only 37%. As a comparison with literature [12] the same $Ni/Al_2O_3$ catalyst was used in citral hydrogenation in hexane as a solvent. Citronellal selectivity was 93% even at 90% conversion in citral hydrogenation at 60 °C and 10 bar in a batch reactor. The lower selectivity in the current work can be explained by the use of a more hydrophilic solvent 2-pentanol as well as a higher reaction temperature (70 °C) both favoring formation of alcohols, citronellol and 3,7-dimethyloctanol. Pressure increase both in this work and in [12] enhanced the formation of consecutive products.

## 5. Rate equations and kinetic modeling

In citral hydrogenation both parallel and consecutive reactions occur simultaneously. The following products were obtained under the reaction conditions: citronellal, citronellol, geraniol, isopulegol, nerol, 3,7-dimethyloctanal and 3,7-dimethyloctanol. Some of these products were only formed in very low quantities and thus the reaction scheme shown in Eq. (1) (Fig. 1) has been applied. Since the working hypothesis (see Section 1) for applying Eq. (4) is that the product selectivities are unaffected by the catalyst bulk density, only the results at 50 °C with liquid phase drainage can be involved in kinetic modeling.

A component A reacts according to Eq. (1) and the initial concentrations of the reaction products B, C and D were assumed to be zero. Taking into account the stoichiometry in (11) the reactor mass balance Eq. (8), the concentration changes as a function of time can be written as

$$\frac{\mathrm{d}c_\mathrm{A}}{\mathrm{d}t} = -r_1\rho_\mathrm{B}, \qquad \frac{\mathrm{d}c_\mathrm{B}}{\mathrm{d}t} = (r_1 - r_2)\rho_\mathrm{B},$$

$$\frac{\mathrm{d}c_\mathrm{C}}{\mathrm{d}t} = (r_2 - r_3)\rho_\mathrm{B}, \qquad \frac{\mathrm{d}c_\mathrm{D}}{\mathrm{d}t} = r_3\rho_\mathrm{B} \tag{11}$$

Concentration profiles for different experiments with and without drainage of liquid phase for the consecutive reactions according to Eq. (1) were simulated with the Modest software [13].

Reaction rates for steps (1), (2) and (3) in Fig. 1 were modeled with the following rate equations:

$$r_1 = \frac{k_1 K_\mathrm{A} c_\mathrm{A}}{1 + K_\mathrm{A}c_\mathrm{A} + K_\mathrm{B}c_\mathrm{B} + K_\mathrm{C}c_\mathrm{C} + K_\mathrm{D}c_\mathrm{D}} \frac{K_\mathrm{H}c_{\mathrm{H}_2}}{1 + K_\mathrm{H}c_{\mathrm{H}_2}} \tag{12}$$

$$r_2 = \frac{k_2 K_\mathrm{B} c_\mathrm{B}}{1 + K_\mathrm{A}c_\mathrm{A} + K_\mathrm{B}c_\mathrm{B} + K_\mathrm{C}c_\mathrm{C} + K_\mathrm{D}c_\mathrm{D}} \frac{K_\mathrm{H}c_{\mathrm{H}_2}}{1 + K_\mathrm{H}c_{\mathrm{H}_2}} \tag{13}$$

$$r_3 = \frac{k_3 K_\mathrm{C} c_\mathrm{C}}{1 + K_\mathrm{A}c_\mathrm{A} + K_\mathrm{B}c_\mathrm{B} + K_\mathrm{C}c_\mathrm{C} + K_\mathrm{D}c_\mathrm{D}} \frac{K_\mathrm{H}c_{\mathrm{H}_2}}{1 + K_\mathrm{H}c_{\mathrm{H}_2}} \tag{14}$$

corresponding to the Langmuir–Hinshelwood mechanism. The mechanism is based on an assumption that all the reactants are adsorbed on the active sites of a catalyst surface. Reactions occur only between the adsorbed reactants and molecularly adsorbed hydrogen. Surface reactions are determining the reaction rate in this model while adsorption, desorption steps are assumed to be in quasi-equilibria.

The application of Langmuir–Hinshelwood mechanism implies that the product selectivities are independent of the catalyst bulk density. Since this was not the case for all the data sets in citral hydrogenation, parameter estimation results only for experiments at 50 °C are presented below.

Hydrogen concentration in 2-pentanol was obtained from literature [2] and an equation for hydrogen solubility was approximated at 70 °C as follows:

$$x_{\mathrm{H}_2} = 0.0002\, p_{\mathrm{H}_2} - 0.0002 \tag{15}$$

with linear regression analysis. A linear model was applied for hydrogen solubility. The data of hydrogen solubility at temperatures 50 and 100 °C in 1-pentanol, which resembles very much 2-pentanol [2], have been taken from literature [14] and plotted together with the solubility of hydrogen at 70 °C in 2-pentanol [2] (the plot is not depicted here). It turned out that the hydrogen solubility in a temperature range 50–100 °C below 21 bar did not have large temperature dependency.

In numerical data fitting the rate constants and adsorption parameters were determined with nonlinear regression minimizing the objective function ($Q$) defined as a difference between experimental concentrations ($c_i$) and estimated concentrations by using mass balances ($\hat{c}_i$):

$$Q = \sum (c_i(t) - \hat{c}_i(t))^2 \tag{16}$$

In the parameter estimation Levenberg–Marquardt method, simplex method or combination of them were applied by using software Modest [13]. The quality of the model is illustrated by the degree of explanation ($R^2$) defined as:

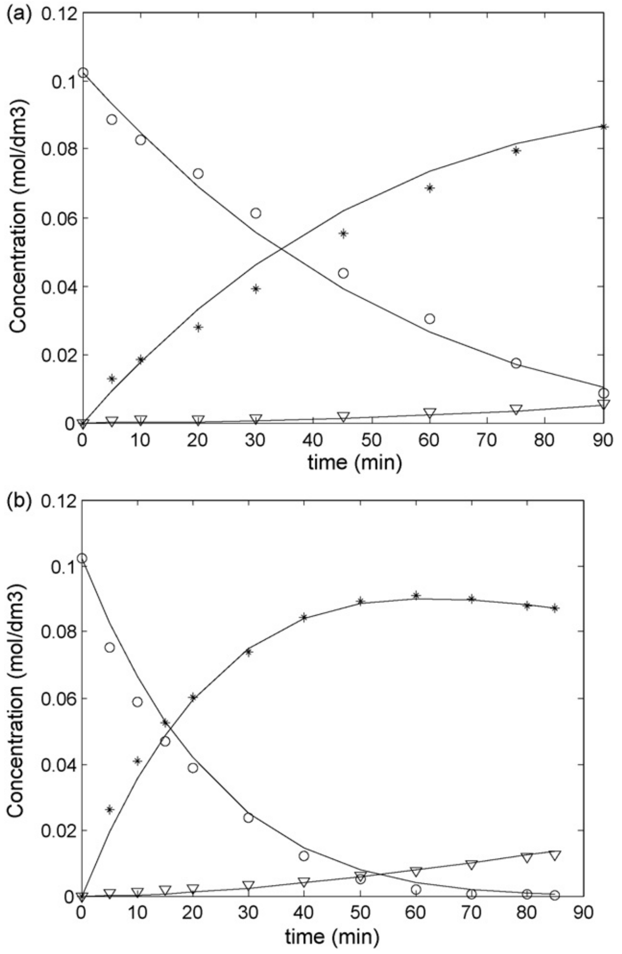

Fig. 6. Kinetic model (–) and experimental data at 50 °C with drainage of the liquid phase at hydrogen pressure of (a) 5 bar and (b) 10 bar. Symbols: citral (◯), citronellal (+), citronellol (*) and 3,7-dimethyloctanol (▽).

$$R^2 = 1 - \frac{\sum (c_{i,\mathrm{exp}} - \hat{c}_{i,\mathrm{mean}})^2}{\sum (c_{i,\mathrm{exp}} - \bar{c}_{i,\mathrm{mean}})^2} \tag{17}$$

where $\bar{c}_{i,\mathrm{mean}}$ is an average of concentrations from the experimental data. A rule of thumb is that degree of explanation should be higher than 95% for a model, which is able to describe the kinetic data accurate enough.

The model fit in the presence of liquid phase drainage from citral hydrogenation at 50 °C is depicted in Fig. 6. In the prelim-

Table 2
Lumped kinetic parameters in citral hydrogenation at 50 °C with liquid drainage of the liquid phase

| Parameter | Estimated parameter | Est. relative standard error (%) |
|---|---|---|
| $k'_1$ | 134 | 1.7 |
| $k'_2$ | 4.96 | 8.8 |
| $k'_3$ | 4.42 | 140.4 |

The degree of explanation $R^2 = 99.3\%$.

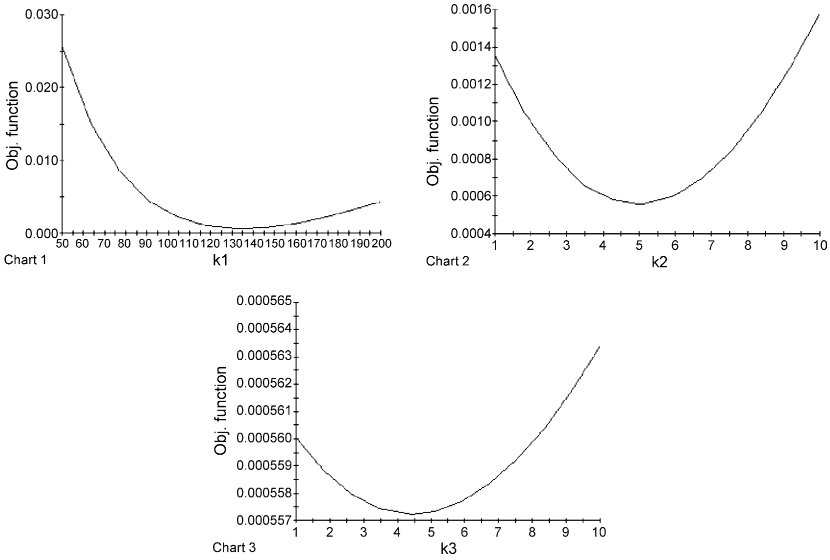

Fig. 7. Sensitivity plots of the estimated parameters.

inary calculations it was shown, that the terms in denominators of Eqs. (12)–(14) containing adsorption coefficients could be neglected leading to the following rate expressions

$$r_1 = k_1 K_\mathrm{A} K_\mathrm{H} c_\mathrm{A} c_{\mathrm{H}_2} = k_1' c_\mathrm{A} c_{\mathrm{H}_2} \tag{18}$$

$$r_2 = k_2 K_\mathrm{B} K_\mathrm{H} c_\mathrm{B} c_{\mathrm{H}_2} = k_2' c_\mathrm{B} c_{\mathrm{H}_2} \tag{19}$$

$$r_3 = k_3 K_\mathrm{C} K_\mathrm{H} c_\mathrm{C} c_{\mathrm{H}_2} = k_3' c_\mathrm{C} c_{\mathrm{H}_2} \tag{20}$$

The lumped kinetic parameters (Table 2), which contain the contributions of both rate and adsorption constants are apparent, since they include also deactivation.

The degree of explanation with the simplified model was 99.3%. The standard errors for $k_1'$ and $k_2'$ were low, while $k_3'$ contained some uncertainty due to the low amounts of 3,7-dimethyloctanol formed at 50 °C (Table 2). Sensitivity analysis illustrated in the form of sensitivity plots for the lumped kinetic parameters (Fig. 7) and the contour plot for $k_1'$ and $k_2'$ (Fig. 8) demonstrate good identifiability of the parameters.

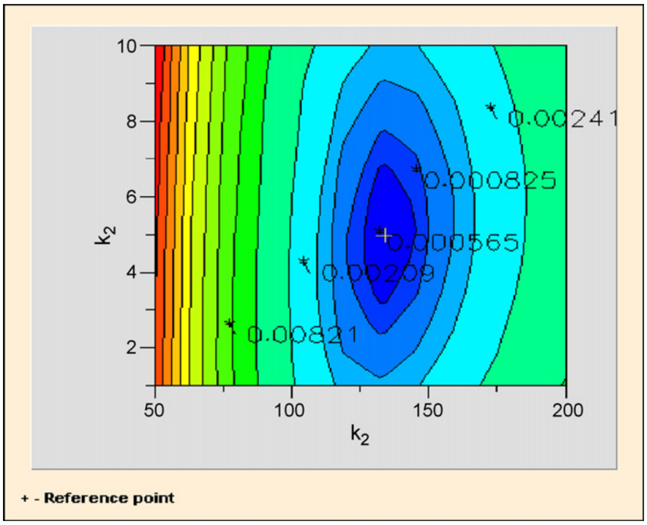

Fig. 8. Contour plot for the parameter $k_1$ and $k_2$.

It should be pointed out here, that the main aim of the current work was to demonstrate a three-phase reactor system working with increasing catalyst bulk density and not modeling the kinetics in citral hydrogenation. Since the kinetic data was not free from catalyst deactivation, the kinetic modeling part remained rather limited and should be investigated in more detail with a larger, more representative data set with the same reactor set-up.

## 6. Conclusions

Kinetics of three-phase citral hydrogenation over a $\mathrm{Ni/Al_2O_3}$ catalyst was investigated in a temperature and pressure range of 50–90 °C and 5–21 bar, respectively. The main aim of this work was demonstrate a reactor set-up, which was operated either in a batch or semibatch mode in respect to liquid phase. In the latter case the liquid phase was continuously pumped out from the reactor. In this manner the catalyst bulk density increased during the hydrogenation experiment. Such operation mode gives a possibility to study consecutive reactions with significant difference in their rates resulting in better identifiability of kinetic parameters.

The kinetic data with increasing catalyst bulk density was compared with the data obtained with a constant liquid phase bulk density. It turned out that only partially kinetic data were unaffected by the change of catalyst bulk density. For instance the product selectivities were independent on the catalyst bulk density only at lower temperatures. The results in case of citral hydrogenation should be attributed to well-demonstrated catalyst deactivation in this particular reaction.

The mechanistic kinetic models were derived for consecutive hydrogenation of citral. Due to the varying product selectivity with changing the catalyst bulk density, kinetic modeling was performed for a limited data set, giving good description of experiments.

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