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Kinetics, catalyst deactivation and modeling in the hydrogenation of β-sitosterol to β-sitostanol over microporous and mesoporous carbon supported Pd catalysts

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ABSTRACT

Kinetics of the hydrogenation of β-sitosterol to β-sitostanol is of industrial interest, since the desired product is used for suppressing cholesterol absorption in human body. The main drawback when using microporous Pd/C catalyst in this reaction is catalyst deactivation. In the current work the performance of microporous and mesoporous Pd catalysts in the hydrogenation of β-sitosterol was compared. The catalytic hydrogenations were performed in a shaking batch reactor in 1-propanol as a solvent. With larger amounts of catalyst less catalyst deactivation occurred due to the fact that the catalyst support acted also as an adsorbent. The mesoporous 4 wt.% Pd/C (Sibunit) catalyst showed higher sitosterol conversions and less catalyst deactivation compared to a microporous 5 wt.% Pd/C catalyst. The kinetics of the hydrogenation of β-sitosterol to β-sitostanol was studied over 4 wt.% Pd/C (Sibunit) catalyst at different temperatures between 60 °C and 80 °C and by reusing the catalyst. The origin for catalyst deactivation was poisoning by phosphorus and sulphur, as well as coking. In situ catalyst potential measurements showed that there is a correlation between catalyst deactivation and decreasing catalyst potential with increasing sitosterol conversion. A mechanistic kinetic model including a deactivation factor was successfully applied to this reaction and the kinetic parameters were determined.

1. Introduction

Nowadays, one of the most important problems for human health is high concentration of fats in food. Therefore, a lot of attention was devoted to β-sitostanol, which was proved to suppress cholesterol absorption in human body [1], and it is thus used as a constituent of some margarines available on the consumer market since 1995 [2]. The cholesterol lowering ability of sitostanol is superior to sitosterol, which is available from woody biomass. Furthermore, in margarine the sitostanols are used as esters. The raw material in the hydrogenation step of sitostanol esters production technology is β-sitosterol, a phytosterol being extracted mainly from tall oil pitch [3], which is the tall oil distillation residue. Sitosterol purification before hydrogenation is an essential production step [4]. The main reaction scheme is presented in Fig. 1. There exist more than 40 different phytosterols and typically the raw material from pulp waste streams contains besides β-sitosterol also β-sitostanol, a hydrogenated product of β-sitosterol as well as campesterol and its hydrogenation product campestanol. The difference in β-sitosterol and campesterol is in their side chain structures (Fig. 2).

Hydrogenation of β-sitosterol has been previously investigated over microporous Pd/C [5], Pd supported on polymer fiber [6] and some other Pd supported catalysts [7]. The challenge in industrial hydrogenation of sitosterol has been the catalyst deactivation. The origin for catalyst deactivation has been reported to be e.g. poisoning and sintering of Pd as well as pore blockage and coke formation [7]. Additionally it should be kept in mind, that sitosterol molecule is relatively large compared with the pore sizes in typical supported catalysts and thus when Pd is locating inside the microporous structure it can be partially inaccessible for sitosterol. The aim of the present work was to evaluate catalytic activity of a microporous Pd/C catalyst and compare its performance to that of a mesoporous Pd/C (Sibunit) in hydrogenation of β-sitosterol.

2. Materials and methods

2.1. Catalyst synthesis and characterization

4 wt.% Pd/C catalyst was synthesized by using Sibunit as the support material. The catalyst was prepared by hydrolysis of H_2PdCl_4 at pH 5–6 to yield so-called polynuclear hydroxocomplexes of palladium followed by their adsorption on carbon and increasing of

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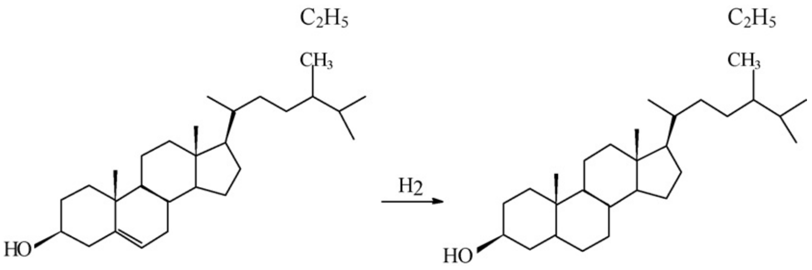

Fig. 1. Reaction scheme for β-sitosterol hydrogenation.

pH slurry up to Na/Pd ratio 1:2 [8]. Prior to the catalyst preparation, carbon was pre-oxidized by treating it by 5 wt% HNO_3 during 17 h, then washed by distilled water and dried. As a reference catalyst 5 wt.% Pd/C (Aldrich) was used.

The specific surface area of the catalysts was studied by nitrogen adsorption using Carlo Erba Instruments. The metal dispersion was measured by pulse CO-chemisorption (Micromeritics Autochem 2901). The catalyst was prereduced at 100 °C for 30 min with flowing hydrogen (AGA, 99.9995) and flushed with helium for 45 min. Thereafter the catalyst was cooled to ambient temperature and the CO-pulse chemisorption measurement was started by using 10 vol% CO in helium (AGA). The stoichiometric relationship between Pd and CO is assumed to be unity [9].

2.2. Reactor setup and analysis

The kinetic experiments were performed in a shaking reactor using 1-propanol as a solvent. The volume of the liquid phase was 110 mL and the pressure was set to 4 bars. The raw material according to the mass spectrometer results contained: 82 wt.% β-sitosterol, about 7 wt.% campesterol, 9 wt.% β-sitostanol and 1 wt.% campesterol. The β-sitosterol hydrogenation was carried out in the presence of several supported Pd catalysts. The samples were withdrawn periodically from the reactor which operated in a temperature range of 60–80 °C at 3.7 bar hydrogen. After addition of an internal standard solution consisting of heneicosanoic acid and betulinol, the reaction mixture was evaporated under nitrogen and silylated at 60 °C for 45 min with BSTFA-TMCS-pyridine solution and analyzed by a GC equipped with a HP-1 column (length 25 m, internal diameter 0.20 mm, film thickness 0.11 μm) using hydrogen as carrier gas and FI detector. The split ratio was 24:1. The products were identified with GC–MS. The catalyst potential was measured in situ using an Ag, AgCl/2 M LiCl electrode.

Additionally, ICP-OES (Inductively coupled plasma optical emission spectrometry) and IC (ion chromatography) techniques were used to detect the presence of chlorine and another potential poisoning agents in the raw material. For this purpose, a sample of 0.1 g sitosterol was immersed in 5 ml of concentrated HNO_3 (65%) and 1 ml H_2O_2 (30%). Later on, this solution was digested in a microwave oven (Anton Paar, Multiwave 3000) and diluted to 100 ml with deionized water. The ICP-OES was performed in a PerkinElmer, Optima 5300 DV and the target was to see the presence of S and P. Moreover, IC was performed in Waters, HPLC 2690 with conductometric detector and suppressor, using a Dionex IonPac AS22 column and the target was to investigate the presence of Cl^-, SO_4^{2-} and PO_4^{3-}.

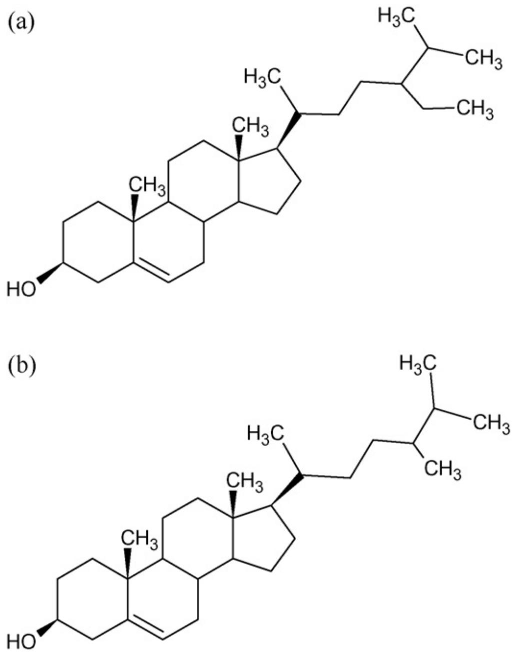

Fig. 2. Chemical structures of (a) sitosterol and (b) campesterol.

3. Results and discussion

3.1. Catalyst characterization results

The average Pd particle sizes determined by CO-chemisorption were for Pd/C (Sibunit) and for Pd/C (Aldrich) 3.1 nm and 5.4 nm, respectively. The specific surface areas for the former and the latter catalysts are given in Table 1, which shows that the specific surface area of the used Pd/C (Aldrich) decreased by 68% indicating that one reason for catalyst deactivation was coking (see Section 3.2). The pore size distribution of Pd/C (Aldrich) and Pd/C (Sibunit) is given in Table 2. The average pore sizes for Pd/C (Aldrich) and for Pd/C (Sibunit) were 2–3 nm and 7 nm, respectively. The microporous Pd/C (Aldrich) could thus be more easily prone to coking than Pd/C (Sibunit) when comparing the average pore size to the size of the reactant molecule.

Temperature programmed desorption of hydrogen showed the total amount of hydrogen desorbed from Pd/C (Aldrich) was 88% of the value for Pd/C (Sibunit) (Fig. 3, Table 3). The maximum temperature for hydrogen desorbed from Pd/C (Aldrich) was about 170 °C, whereas two maximum temperatures were obtained for Pd/C (Sibunit), i.e. 130 °C and 338 °C (Table 3). Although less hydrogen was desorbed at relatively low temperature over Pd/C (Sibunit)

Table 1
Specific surface areas for catalysts.

Catalyst	Specific surface area ($m^2/g_{cat.}$)	
	BET	Dubinin
5 wt% Pd/C (Aldrich)	974	1310
5 wt% Pd/C (Aldrich), used	313	439
4 wt% Pd/C (Sibunit)	243	286

Table 2
Characterization results of the catalyst pore size distribution. Relative volumes (%).

Catalyst	Macropores and mesopores			Micropores				
	100–10 (nm)	10–5 (nm)	5–2 (nm)	2.0–1.5 (nm)	1.5–1.0 (nm)	1.0–0.9 (nm)	0.9–0.8 (nm)	0.8–0 (nm)
4 wt% Pd/C (Sibunit)	70	5	25	0	0	0	0	0
5 wt% Pd/C (Aldrich)	39	17	32	2	3	4	3	0

Table 3
Temperature programmed desorption of hydrogen from palladium catalyst.

Catalyst	H_2-TPD					
	Desorbed H_2 below 250 °C[a]	Peak I		Peak II		Total desorbed H_2[a]
		H_2-desorbed[a]	T_{max} (°C)	H_2-desorbed[a]	T_{max} (°C)	
4 wt% Pd/C (Sibunit)	1.2	2.0	130	3.0	338	5.0
5 wt% Pd/C (Aldrich)	1.4	4.4	170			4.4

[a] Amount of hydrogen expressed in μmol/g of catalyst.

TPD data did not correlate directly with the catalytic performance (see Section 3.3.2).

3.2. *Characterization of raw material*

The raw material contained according to ICP-OES 300 ppm sulfur and 230 ppm phosphorus, respectively. In addition, traces of chloride were found (50 ppm). These compounds can partially affect the catalyst performance (see below).

3.3. *Qualitative kinetic results*

3.3.1. *Tests with different catalyst mass*

The only reaction products confirmed by GC-MS in a sample from sitosterol hydrogenation at 70 °C over Pd/C (Aldrich) and over Pd/C (Sibunit) were sitostanol and campestanol, since neither sitostane no sitostanone were found. The reaction exhibited thus complete selectivity towards sitostanol and campestanol.

Preliminary experiments using different ratios of reactant to catalyst (450:1, 18:1 and 9:1) were performed with very small catalyst particles (<45 μm) in order to see the effect of gas liquid mass transfer limitations. When plotting the molar fraction of sitosterol as a function of normalized abscissa, time multiplied by catalyst mass these three curves should coincide. This was not, however, the case. The largest conversion of sitosterol (90%) was achieved when using the largest catalyst amount, whereas with 250 mg and with 100 mg of catalysts the conversions after 160 min were 83% and 52%, respectively (Fig. 4). This result indicated that catalyst deactivation was less prominent when using a higher catalyst amount with the catalyst acting as an adsorbent. This is clearly visible from the SEM/EDXA data from the analysis of the relative amounts of sulphur and phosphorus in fresh and spent Pd/C (Aldrich) samples (Table 4). The ratio of sulphur to carbon increased by factor 2.3 in the spent catalyst compared to the fresh one. Analogously phosphorus to carbon ratio increased from zero to the level of 1.3×10^{-2}.

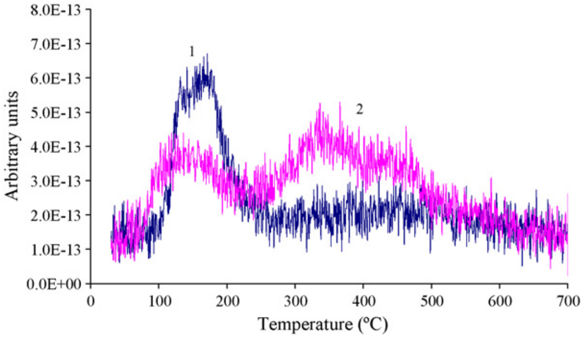

Fig. 3. Hydrogen TPD from (1) Pd/C (Aldrich) and (2) Pd/C (Sibunit).

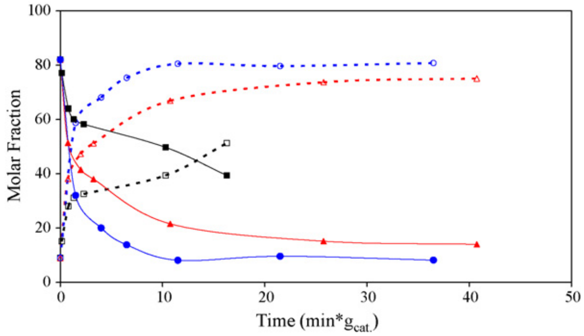

Fig. 4. Kinetics in sitosterol hydrogenation using different amounts of 5 wt.% Pd/C (Aldrich) as a catalyst at 70 °C and under 3.7 bar hydrogen. Catalyst particle size was below 45 μm. Symbols: (○) 500 mg, (▲) 250 mg and (■) 100 mg. Solid symbol sitosterol and open symbol sitostanol.

Catalyst deactivation occurred over 4 wt.% Pd/C (Sibunit) analogously to Pd/C (Aldrich) catalyst in sitosterol hydrogenation at 70 °C under 3.7 bar hydrogen in 1-propanol (Fig. 5a). The conversions of sitosterol after 160 min reaction time with 100 mg and 450 mg of catalyst were 80% and 96%, respectively.

Catalyst potential was recorded in situ during the sitosterol hydrogenation and plotted against sitosterol conversion using either 100 mg or 450 mg of Pd/C (Sibunit) catalyst (Fig. 5b). The catalyst potential decreased fast with increasing sitosterol conversion, when only 100 mg of catalyst was used. In the case of a larger amount of catalyst, i.e. 450 mg, under conditions, when the reaction proceeded faster than with a lower catalyst amount, the catalyst potential remained constant until the conversion level of 93%. At constant pH the change in the electrode potential is determined by the change in the activity of adsorbed hydrogen. When a certain equilibrium exists between the dissolved and adsorbed hydrogen during the catalytic reaction, the activity of adsorbed hydrogen is constant and Δ*E* is equal to zero. At high conversion of sitosterol

Table 4
Energy dispersive X-ray analysis results for 5 wt% Pd/C (Aldrich).

	EDXA			
	S/C	S/Pd	P/C	P/Pd
Fresh catalyst	1.2×10^{-3}	1.3×10^{-2}	0	0
Spent catalyst	2.8×10^{-3}	6.6×10^{-2}	1.3×10^{-2}	2.2×10^{-1}

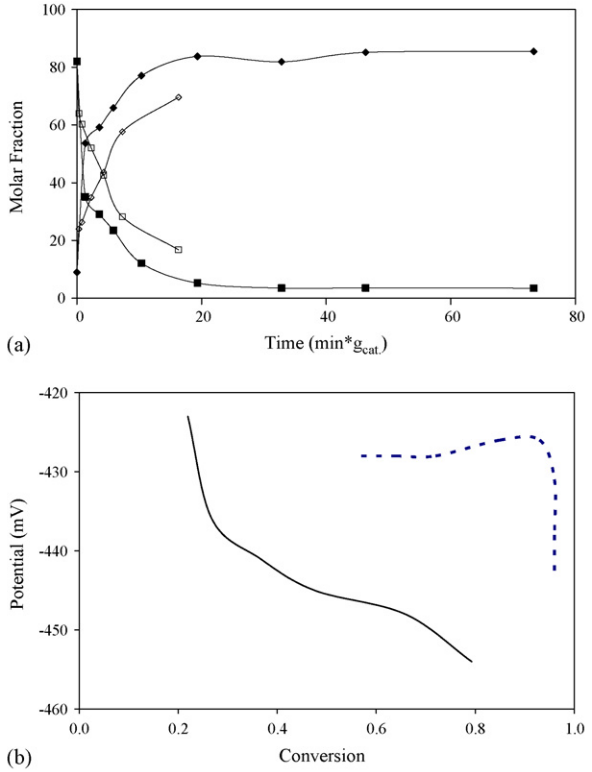

Fig. 5. (a) Kinetics in sitosterol hydrogenation over 4 wt.% Pd/C (Sibunit) at 70 °C and 3.7 bar hydrogen in 1-propanol. Symbols: sitosterol (■) 450 mg cat., (□) 100 mg cat. and sitostanol (♦) 450 mg cat. and (◊) 100 mg cat. (b) Catalyst potential: 450 mg cat. dashed line, 100 mg cat. solid line. Catalyst particle size was below 45 μm.

for the case of larger catalyst amounts there is no more sitosterol present on the surface, which is then completely occupied by hydrogen. When the catalyst activity declines due to coking during the reaction quasi-equilibrium between dissolved hydrogen and adsorbed hydrogen does not hold and the catalyst potential changes significantly.

3.3.2. *Comparison of microporous and mesoporous Pd/C catalysts*

The comparison of the kinetics in sitosterol hydrogenation over microporous 5 wt.% Pd/C (Aldich) and mesoporous 4 wt.% Pd/C (Sibunit) is shown in Fig. 6. Both higher initial rate and higher conversion after 160 min were achieved over the latter catalyst. The sitosterol conversions after 160 min were for Pd/C (Aldrich) and Pd/C (Sibunit) 52% and 82%, respectively. When comparing the initial rates with the Pd dispersion and with the hydrogen TPD results (Section 3.1), it can be seen that the initial hydrogenation rates were correlating neither with the Pd particle sizes nor with the hydrogen TPD results. On the other hand, the sitosterol molecular size is quite large in comparison to micropores, which is thus the most determining factor for the catalyst activity.

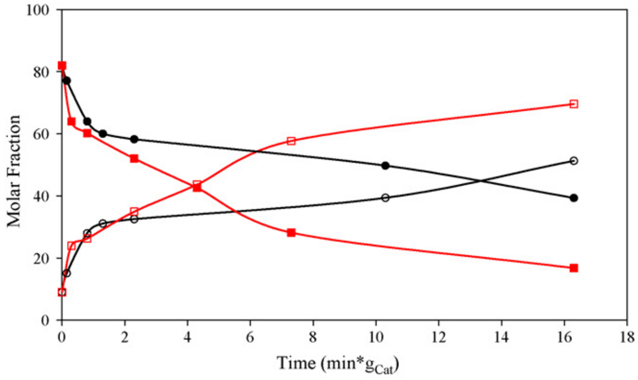

Fig. 6. Kinetics in sitosterol hydrogenation over 5 wt.% Pd/C (Aldrich) and over 4 wt.% Pd/C (Sibunit) at 70 °C and under 3.7 bar hydrogen. The reactant to catalyst ratio was 450:1 and the catalyst particle size was 45 μm. Symbols: (■) sitosterol and (□) sitostanol over Pd/C (Sibunit), (●) sitosterol and (○) sitostanol over Pd/C (Aldrich).

Catalyst deactivation was more prominent over the microporous Pd/C (Aldrich) catalyst compared to the Pd/C (Sibunit). This result is expected, when considering that the sitosterol molecule is quite large and there are micropores in Pd/C (Aldrich), whereas only mesoporous are present in Pd/C (Sibunit) (Table 2). Additionally both coking and poisoning of Pd occur under the current reaction conditions.

3.3.3. *Effect of temperature on the kinetics of sitosterol hydrogenation over mesoporous Pd/C*

The effect of temperature was investigated in sitosterol hydrogenation over 4 wt.% Pd/C (Sibunit) using reactant to catalyst ratio of 450:1 under 3.7 bar hydrogen (Fig. 7). The hydrogenation rate increased with increasing temperature. It should, however, be noted that catalyst deactivation was quite prominent, since even

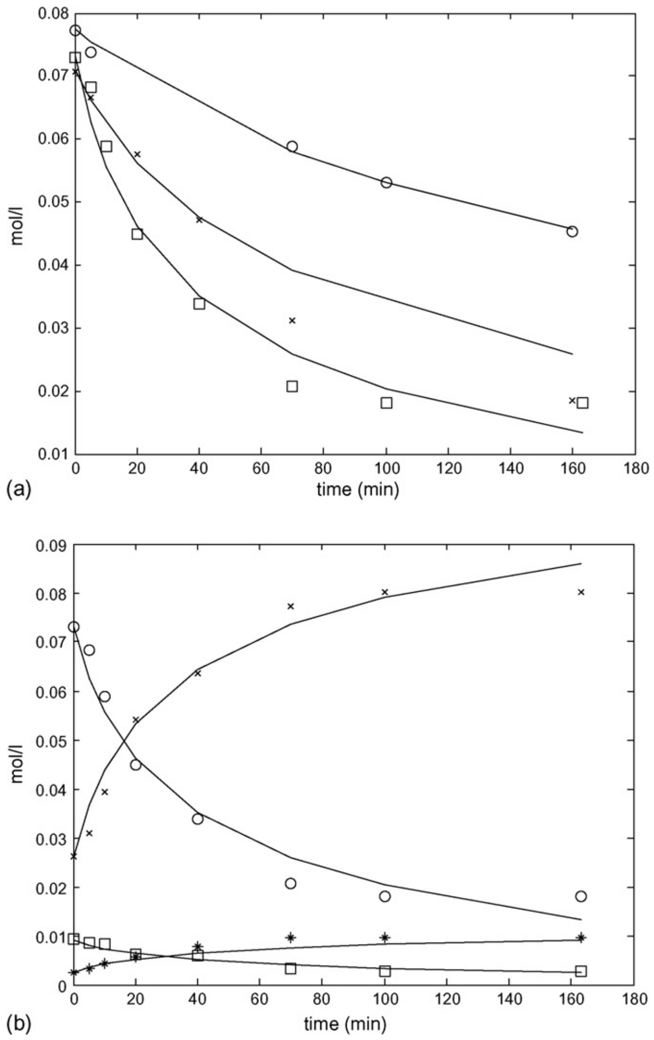

Fig. 7. (a) Effect of temperature on the sitosterol hydrogenation over 4 wt% Pd/C (Sibunit). Conditions: reactant to catalyst ratio 450:1, hydrogen pressure 3.7 bar, catalyst particle size below 45 μm. Solid line is model fitting, points are experimental data points, 60 °C (○), 70 °C (×) and 80 °C (□). (b) Fit of model to experimental data sitosterol (○), sitostanol (×), campesterol (□) and campesterol (*) at 80 °C.

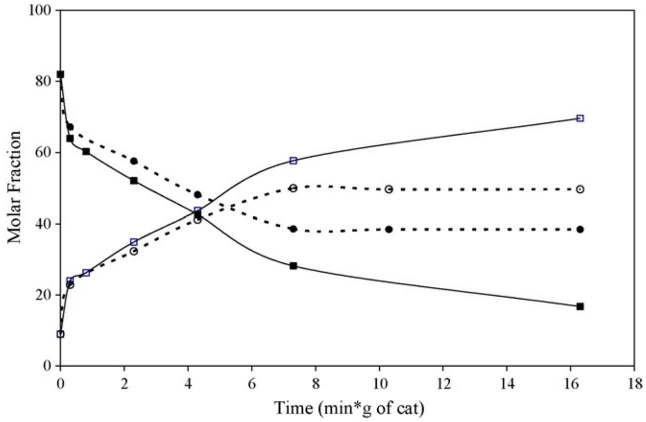

Fig. 8. Effect of the initial sitosterol concentration on the hydrogenation kinetics over 4 wt.% Pd/C (Sibunit) at 70 °C and under 3.7 bar hydrogen. Catalyst particle size was below 45 μm. Symbols: 0.05 mol/l dashed line, 0.1 mol/l solid line, sitosterol (●), sitostanol (○), 0.05 mol/l solid line, sitosterol (■) and sitostanol (□).

at the highest reaction temperature, 80 °C, only 80% conversion of sitosterol was achieved within 160 min. Additionally catalyst deactivation increased with increasing temperature, since the conversion obtained at 70 °C was equal to that achieved at 80 °C. The activation energy was determined as explained in Section 3.4.

3.3.4. Effect of sitosterol initial concentration

Two different initial sitosterol concentrations in sitosterol hydrogenation were investigated over 4 wt% Pd/C (Sibunit), 0.05 mol/l and 0.1 mol/l using 100 mg of catalyst (Fig. 8). Slightly higher initial hydrogenation rates and higher conversion of sitosterol after prolonged reaction times were achieved with higher initial sitosterol conversion. The initial hydrogenation rates and the conversion levels after 160 min were for the former and latter one 0.5 mmol/min/$g_{cat.}$ and 0.6 mmol/min/$g_{cat.}$ as well as 54% and 79%, respectively. This result indicates that despite the catalyst deactivation the positive effect of the initial sitosterol concentration on hydrogenation activity was larger than the negative effect of catalyst deactivation.

3.3.5. Reuse of mesoporous Pd/C catalyst in sitosterol hydrogenation

Catalyst deactivation was quite dominant in the catalyst reuse tests performed at 70 °C under 3.7 bar hydrogen over Pd/C (Sibunit) catalyst (Fig. 9a). Conversion of sitosterol after 160 min after the first, the second and the third runs with the same catalyst was 96%, 72% and 54%, respectively. The catalyst potentials were measured in situ in these tests and shown as a function of conversion in Fig. 9b. The catalyst potential for the fresh catalyst was constant with increasing sitosterol conversion up to 92% level, thereafter it decreased and simultaneously no more sitosterol was converted. In the first and second reuse of the catalyst the negative slope for the ratio between the potential decreases to the molar fraction of sitosterol became more steep for the latter case. The constant catalyst potential indicates that the hydrogen coverage on the catalyst surface was constant. When the catalyst potential decreased, more hydrogen was accumulated on the surface due to the absence of the hydrogenation reaction or due to the declined hydrogenation rate. The catalyst deactivation was, however, very extensive already after 3 min of reaction time and there was no catalytic activity after 73 min with 0.05 mol/l sitosterol.

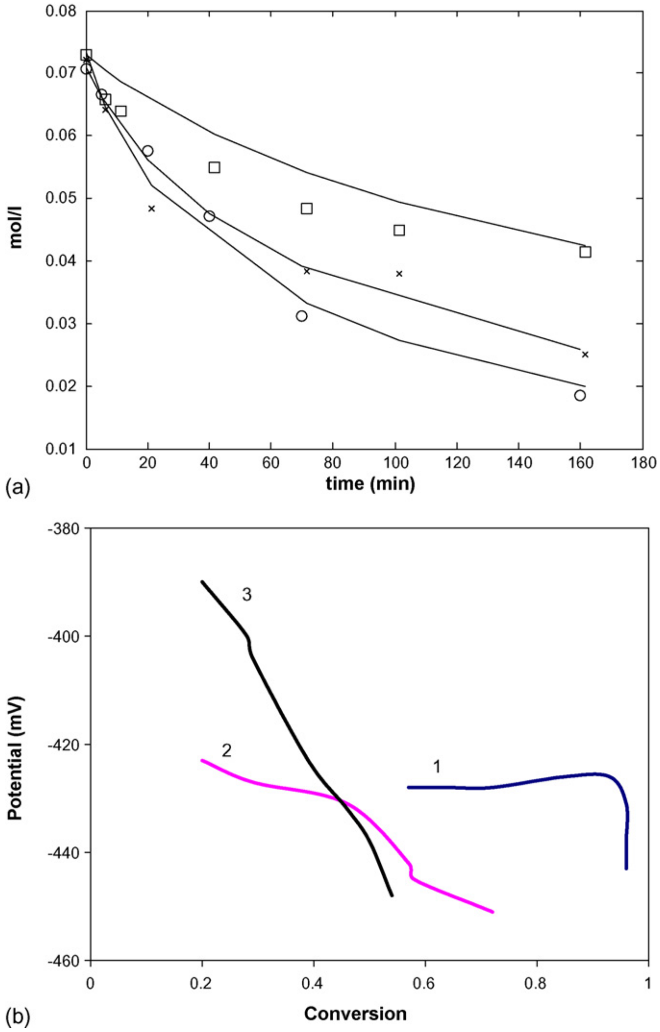

Fig. 9. (a) Kinetics in sitosterol hydrogenation over 4 wt.% Pd/C (Sibunit) at 70 °C and 3.7 bar hydrogen in 1-propanol. Symbols: (○) fresh catalyst, (×) used once and (□) used twice, solid line is model fitting, points experimental values. (b) Catalyst potential: 4 wt. Pd/C (Sibunit): (1) fresh, (2) used once and (3) used twice in sitosterol hydrogenation. Catalyst particle size was below 45 μm.

3.4. Kinetic modeling

3.4.1. Kinetics

The kinetic modeling was based on the following hypothesis: molecularly adsorbed hydrogen was assumed to react on the catalyst surface with adsorbed sterol species. Furthermore, adsorption of hydrogen and the organic molecules was supposed to be in quasi-equilibria and essentially of non-competitive nature [5]. The mass transfer limitations were suppressed due to efficient stirring and small size of catalyst particles, thus, the effectiveness factor was approximated to unity. As mentioned above the model includes equilibrium for sitosterol adsorption giving:

$$A + {}^{*} \Leftrightarrow A^{*}$$

$$K_a = \frac{\theta_a}{c_a \theta_0} \rightarrow \theta_a = K_a c_a \theta_0 \qquad (1)$$

where K_a represents the adsorption equilibrium constant, θ_0 is the fraction of vacant sites available for the adsorption and θ_a is the sitosterol coverage. Moreover, from the balance equation for the sites,

$$1 = \theta_a + \theta_c + \theta_0 \qquad (2)$$

explicit expressions for coverages are obtained:

$$\theta_i = \frac{K_i c_i}{1 + \sum K_i c_i} \tag{3}$$

where index i denotes the components present in the reaction mixture (sitosterol, sitostanol, campesterol and campestanol). It can be assumed that desorption of sitostanol and campestanol is fast that their coverage can be neglected.

The rates of the hydrogenation steps for sitostanol and campestanol formation are respectively given by:

$$r_1 = k_1' \frac{c_a}{G} \quad \text{and} \quad r_2 = k_2' \frac{c_c}{G} \tag{4}$$

where G is defined as

$$G = 1 + K_a c_a + K_c c_c \tag{5}$$

Here a stands for sitosterol and c for campesterol. The lumped constants k_1' and k_2' incorporate respectively also adsorption constants K_a and K_c, as well as hydrogen adsorption term. Since the adsorption terms in Eq. (5) were shown to be very small compared to unity in the preliminary data fitting, the final modeling was performed utilizing the first order model.

3.4.2. Reactor model

The mass balance for a liquid-phase component (i) in a batch reactor was written as

$$\frac{dc_i}{dt} = \rho_E r_i \tag{6}$$

where r_i is the reaction rate and ρ_E is the catalyst bulk density ($\rho_E = m_{\text{cat}}/V_{\text{liq}}$). Moreover, due to the presence of deactivation, an additional term is added to Eq. (6):

$$\frac{dc_i}{dt} = e^{-K_d \times n_e} \rho_E \nu_i r_i \tag{7}$$

where K_d and n_e stand for the deactivation factor and the overall catalyst exposure (amount of moles reacted) to the reaction mixture, respectively.

The modified Arrhenius equation gives the dependence of the kinetic constants on the temperature. The activation energy of the reaction i, E_{ai} and the pre-exponential factor A_i are the parameters of this equation. Referring the exponential term to an average temperature for the experiments, T_{mean}, the model is optimized (orthogonalization or centralization of the experiments) [10].

$$k_i = A_i \times e^{-E_{ai}/R((1/T)-(1/T_{\text{mean}}))} \tag{8}$$

3.4.3. Parameter estimation

The MODEST software using a combined simplex-Levenberg–Marquardt method was chosen to estimate the parameters of the model [11]. Non-linear regression analysis estimates the unknown parameters of the model. Five parameters were estimated, including the activation energy of the two hydrogenation reactions, the pre-exponential factors and the deactivation factor.

The validity of the model is determined by the closeness of the experimental data and the values predicted by the model. Regression analysis is based on the minimization of an objective function (Q). The sum of residual squares is the most common criteria:

$$Q = \sum (c_{i,\text{exp}} - c_{i,\text{calc}})^2 w_i \tag{9}$$

where $c_{\text{i,exp}}$ and $c_{i,\text{calc}}$ denote the experimental and calculated concentrations of the components, respectively. The weight factor (w_i) was set to 1 for all the experimental points. The goodness of the fit is determined with the R^2-coefficient. It compares the residuals given by the model to the residual of the model using the average of all data points:

$$R^2 = 1 - \frac{\sum (c_{i,\text{exp}} - c_{i,\text{model}})^2}{\sum (c_{i,\text{exp}} - c_{i,\text{mean}})^2} \tag{10}$$

Table 5
Estimated parameters.

Parameter	Parameter value	Error (%)
A1	0.0146 min^{-1}	4.6
A2	0.00838 min^{-1}	21.1
Ea1	91.7 kJ/mol	4.8
Ea2	124 kJ/mol	25.8
n_d	270 mol^{-1}	3.1

$T_{\text{mean}} = 70\,^\circ\text{C}$.

The parameters are listed in Table 5. The degree of explanation was 98.91%. The fit of the model to experimental data is shown in Fig. 7a (temperature influence), Fig. 7b (fit of model to all components) and Fig. 9a (deactivation), confirming rather good correspondence between experimental and predicted values.

4. Conclusions

Microporous and mesoporous Pd/C catalysts were investigated in β-sitosterol hydrogenation in a shaking reactor. The only reaction products detected by GC–MS were β-sitostanol and campestanol, whereas neither sitostane or sitostanone were obtained. In the preliminary experiments using different amounts of catalysts the catalyst deactivation was more prominent with lower catalyst amounts. This result indicated that the catalyst acted as an adsorbent for impurities, therefore when larger catalyst amounts were used, the catalytic activity remained higher for longer time. The origin of catalyst deactivation was poisoning by phosphorus and sulphur, which were present in the raw material. Furthermore, catalyst specific surface area decreased after the catalyst use indicating coking.

In the comparison of the performances of mesoporous 4 wt.% Pd/C (Sibunit) and microporous 5 wt.% Pd/C (Aldrich) the higher conversions were achieved after prolonged reaction times over the mesoporous catalyst, which was selected for kinetic studies. Catalyst deactivation occurred also in the mesoporous catalyst, however its activity was kept relatively high for a longer time due to its larger pore size. The catalyst electrochemical potential was constant as a function of sitosterol conversion during the period, when the catalyst was very active indicating constant hydrogen coverage. When catalyst deactivation was very prominent, the catalyst potential decreased with increasing sitosterol conversion, which could be related to catalyst deactivation.

Effects of temperature and initial sitosterol concentration were investigated in sitosterol hydrogenation over 4 wt.% Pd/C (Sibunit). The reaction proceeded faster with a higher initial sitosterol concentration conforming a positive reaction order with respect to sitosterol. The hydrogenation rate increased, as expected, with increasing temperature over 4 wt% Pd/C (Sibunit). The catalyst deactivation was more prominent at 80 °C compared to 70 °C. Catalyst reuse experiments revealed that there is a continuous deactivation occurring as a function of catalyst exposure. Kinetic constants and activation energy were determined by using a simple first order kinetic model including a deactivation factor.

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