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Inverse temperature dependence due to catalyst deactivation in liquid phase citral hydrogenation over Pt/Al_2O_3

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Abstract

Citral hydrogenation was studied over a Pt/Al_2O_3 catalysts in cyclohexane and in 2-pentanol. Several kinetic trends, which were correlated to catalyst deactivation, were achieved. Accumulation of *trans* isomers in both citral and in unsaturated alcohols was visible under deactivating conditions. The further hydrogenation of citronellal was nearly totally inhibited due to catalyst deactivation, whereas nerol, geraniol and citronellol formation were enhanced at higher temperatures and pressures. The main unusual kinetic phenomena in citral hydrogenation in 2-pentanol were, first, a maximum observed in the initial hydrogenation rates as a function of temperature caused by catalyst deactivation and, second, a minimum in citral conversion after prolonged reaction times. The reason for these unusual kinetic phenomena is decarbonylation reaction occurring during hydrogenation, i.e. formation of CO, which was confirmed by temperature programmed desorption of geraniol from a reduced Pt/Al_2O_3 catalyst.

Keywords: Deactivation; Kinetics; Hydrogenation; Citral

1. Introduction

Typically in three phase hydrogenations of α,β-unsaturated aldehydes the reaction rates increase with increasing temperatures [1]. In some cases it has been difficult to determine initial hydrogenation rates in a reliable way especially at higher temperatures due to fast catalyst deactivation, like in nerol (n) hydrogenation [2]. According to our knowledge there is only one publication, in which inverse dependence between the initial hydrogenation rate and temperature has been reported in citral hydrogenation over Pt/SiO_2 catalyst [3]. In that study a kinetic model was developed for the decreasing initial hydrogenation rate with increasing temperature and the phenomenon was explained by catalyst deactivation due to citral decarbonylation. No catalyst characterization was, however, presented. Moreover, the analysis of selectivity and its dependence on deactivation was somewhat limited, as mainly geraniol/nerol (geraniol g, nerol n) and citronellal (cal) were obtained. No data on *cis*/*trans* citral and geraniol/nerol ratio were provided.

Citral hydrogenation is a complex reaction, where the desired product, citronellol (col), is formed as a second product both from citronellal and unsaturated alcohols, nerol and geraniol (Fig. 1) [10]. Another valuable product from citral hydrogenation is menthol [14], which can be hydrogenated from (−)-isopulegol [13]. Citral can be hydrogenated to citronellal with the yield of 87.3% over a Pd/C catalyst at 353 K and 1.0 MPa hydrogen [4], whereas over 91% yields of nerol and geraniol were obtained over a bimetallic Ru-Fe/C catalyst at 353 K and 2.0 MPa [5]. Citronellol was prepared with the yield of 90% via catalytic hydrogenation of citral at 413 K and 10.1 MPa over a $CuO\text{-}Cr_2O_3$ catalyst containing also small amounts of MnO_2 and BaO [6].

In order to obtain higher yields of the consecutive products the batch reactor was operated in a pumping mode via pumping liquid phase continuously out from the reactor during the reaction. In this way the catalyst bulk density was increased as a function of time since the catalyst amount remained constant during the reaction.

Catalyst deactivation in citral hydrogenation has been observed over several catalysts, like Ni/SiO_2 [7], Ni/Al_2O_3 [7] and Ru/Al_2O_3 [8]. Typically the kinetics followed Arrhenius type temperature dependency. In case of nerol hydrogenation, however, an enhanced selectivity as a function of conversion was observed with increasing reaction temperature [2]. In citral hydrogenation over Pt/SiO_2 the main products besides citronellal were nerol and geraniol being together about 80% at

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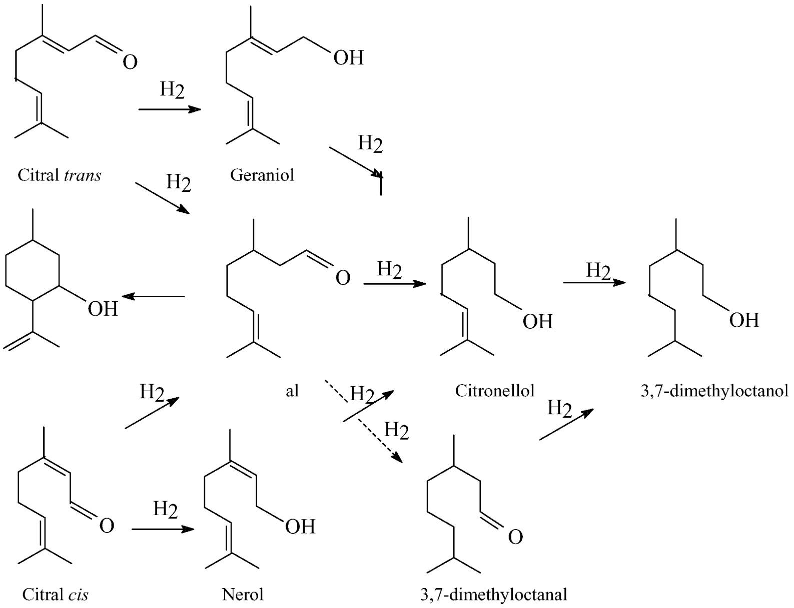

Fig. 1. Reaction scheme in citral hydrogenation.

373 K and 2.0 MPa at 40% conversion in hexane [3]. This paper was thus reporting mainly the two primary parallel reaction routes.

The aim in this work was to investigate unusual kinetics in citral hydrogenation over Pt/Al_2O_3 catalyst yielding large amounts of different parallel and consecutive products. When Pt is an active metal in the catalyst substantial amounts of nerol and geraniol together with citronellal are formed as primary parallel products followed by parallel formation of citronellal and 3,7-dimethyloctanal (dnal) in the second step. The consecutive products are citronellol and 3,7-dimethyloctanol (dmol). Thus in this work the kinetics in complex citral hydrogenation over Pt/Al_2O_3 catalyst is reported in detail and an emphasis is put on the kinetic trends caused by catalyst deactivation. Moreover, the origin of catalyst deactivation was studied via characterization of spent catalysts.

2. Experimental

2.1. Reactor set-up

Citral (Alfa Aesar, 97% with equal initial amounts of *trans* and *cis* citral) hydrogenation was carried out in a batch reactor, where liquid phase was pumped continuously out from the reactor with a constant rate of 1 g/min. The outcoming liquid phase was continuously fed on to a balance, where its weigh was recorded as a function of time. The catalyst amount in the reactor was kept constant (5 g) during the experiments, since a sinter with 7 μm holes was used in the liquid phase pumping line as well as in the sampling line. The catalyst, 5 wt.% Pt/Al_2O_3 (Strem Chemicals, 78–1660), was reduced in situ prior to the reaction with flowing hydrogen (AGA, 99.999%) at 673 K for 60 min, after which it was cooled to room temperature. Then the deoxygenated solvent, either cyclohexane (99.0%, Lab-Scan) or 2-pentanol (>98%, Merck 807501), containing citral was injected into the reactor, thereafter the reactor was heated up to the desired temperature. The reaction was started when the desired temperature was reached via initiating the stirring (1500 rpm). The high stirring rate facilitated the experiments in the kinetic regime. Typically the initial citral concentration was 0.1 mol/dm^3. The total initial liquid phase volume was 325 cm^3 and it decreased continuously until the final liquid phase volume (185 cm^3) was reached. Experiments were performed under overall pressure of either 2.0 and 4.1 MPa.

2.2. Liquid phase analysis

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 and film thickness 0.50 μm). The following temperature programme was used for analysis: 393 K (1 min); 0.30 K/min; 395 K (1 min); 3 K/min; 399 K (1 min); 20 K/min; 473 K (16 min). The injector and the detector temperatures were 523 and 553 K, respectively. Helium (AGA, 99.996%) was used as a carrier gas. The split ratio was 40. The products were identified with commercial standards: nerol (90%, Fluka 72170), geraniol (Tech., Lancaster 6238), citronellal (93%, Acros Organics 40529100), citronellol (Lancaster 5743), 3,7-dimethyloctanol (99%, Aldrich 30.577-4). (−)-Isopulegol (>99.5%, Fluka 59770) and by using GC–MS equipment (Agilent Technologies 5973, mass selective detector) with a capillary column HP-5 (length 30 m, internal diameter 0.25 mm and film thickness 0.25 μm).

2.3. Catalyst characterization

The metal dispersion was measured by hydrogen chemisorption using an automatic chemisorption apparatus (Sorptometer 1900, Carlo Erba Instruments). Adsorption isotherms were recorded at 298 K within the pressure range of 132–13.2 Pa. The catalyst was reduced at 673 K for 2 h with flowing hydrogen after which it was evacuated at 10 Pa for 60 min at 673 K.

The mean catalyst particle size distribution was measured with a Malvern Zetasizer Iic apparatus by scattering He–Ne light, which was reflected to a catalyst powder–ethanol suspension. The interference figures, which were collected by a Fourier lens, were processed with a computer.

The specific surface areas of the fresh and the spent catalysts were determined by nitrogen adsorption using Sorptometer 1900 (Carlo Erba Instruments). The fresh catalyst was degassed at 573 K in vacuo, whereas 373 K was used in degassing for a spent catalyst in order to avoid the desorption of organic species accumulated on the catalyst surface during hydrogenation.

Temperature programmed desorption (TPD) experiments of spent catalysts were carried out by heating the catalyst under helium (AGA, 99.996%) with a flow rate of 50 cm^3/min and temperature programme 10 K/min up to 923 K (30 min) by using Micromeritics (Autochem 2910) apparatus and analyzing the desorbing gases by a quadrupole mass spectrometer (Balzers Instrument, Omnistar).

In the temperature programmed oxidation (TPO) experiments an analogous treatment was used with oxygen containing gas mixture (5 vol.% O_2, 2 vol.% CO_2 (AGA) and 93% He (AGA, 99.996%)).

Temperature programmed desorption of citral and geraniol were performed in the same apparatures as follows: at first catalyst was reduced in situ with flowing hydrogen at 673 K for 60 min followed by adsorption of either citral or geraniol via bubbling helium through a bottle containing the organic compound at 323 K. The vaporized compound was adsorbed on the catalyst surface with flowing helium (20 cm^3/min) under 30 min, thereafter the physisorbed species were flushed with flowing helium for 30 min. Then the temperature programmed desorption was started by using the same temperature program as above.

3. Results and discussion

3.1. Catalyst characterization results

The mean Pt/Al_2O_3 catalyst particle size was 18.2 μm and Pt dispersion determined by hydrogen chemisorption was 40% [9]. The specific surface area and the pore volume of the fresh catalyst determined by nitrogen adsorption were 95 m^2/g_{cat} and 0.319 cm^3/g_{cat}, respectively. In addition to the characterization of a fresh catalyst also spent catalysts have been studied by nitrogen adsorption and temperature programmed methods and these results are presented in Section 3.2.3, together with the kinetic results from catalyst deactivation.

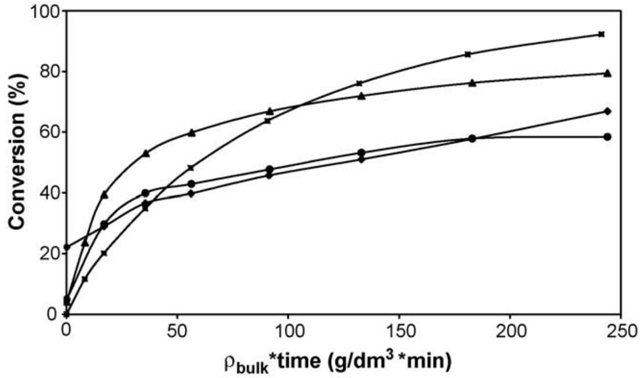

Fig. 2. Conversion of citral as a function of $\rho_{bulk} \times$ time at 2.0 MPa at: (■) 298 K, (▲) 323 K, (●) 343 K and (♦) 373 K in 2-pentanol over Pt/Al_2O_3 catalyst.

3.2. Kinetic results

3.2.1. Reactor set-up and a way to normalize results

The reactor was operated with pumping liquid phase continuously out from the reactor, thereafter the initial hydrogenation rates were calculated from the average amount of citral present in the reactor between the first 0 and 5 min, i.e. taking into account the pumping of citral and solvent. The initial rate is thus the slope when plotting the amount of citral versus time. In the comparison of the catalyst performance in a batch reactor operating with changing catalyst bulk density the correct way to plot kinetic curves is to normalize the abscissa by multiplication of catalyst bulk density and reaction time, i.e. $\rho_{bulk} \times$ time. Initially the catalyst bulk density is:

$$\rho_{0,B} = \frac{m_{cat}}{V_{0,L}} \tag{1}$$

At time *t* the bulk density ρ_B can be written as a function of volumetric flow $\dot{V}$ as follows:

$$\rho_B = \frac{\rho_{0,B}}{1 - (\dot{V}/V_{0,L})} \tag{2}$$

where $V_{0,L}$ denotes the initial liquid phase volume. Catalyst deactivation was more prominent in cyclohexane than in 2-pentanol, since lower conversions were achieved at a given $\rho_{bulk} \times$ time in the previous solvent (Table 1) and thus the kinetic experiments were carried out in 2-pentanol.

3.2.2. Kinetic experiments in 2-pentanol

3.2.2.1. Effect of temperature on initial hydrogenation rates. Citral conversion as a function of $\rho_{bulk} \times$ time is presented in Fig. 2. Initial hydrogenation rates were determined from the initial amounts of citral converted divided by mass of Pt and

Table 1

Comparison of the initial hydrogenation rates, conversions at given $\rho_{bulk} \times$ time = 200 g_{cat}/dm^3 min and amounts of nerol and geraniol as well as citronellal in citral hydrogenation over Pt/Al_2O_3 in 2-pentanol and in cyclohexane at 373 K and 4.1 MPa

Solvent	Initial hydrogenation rate (mmol/min/g_{Pt})	Conversion (%) at a given $\rho_{bulk} \times$ time = 200 (g_{cat}/dm^3 min)	Amount of citronellal (mol%)	Amount of nerol and geraniol (mol%)	Amount of citronellol (mol%)
2-Pentanol	18.7	74	21	31	17
Cyclohexane	18.1	49	22	15	6

Table 2
The initial hydrogenation rates at different temperatures and pressures in citral hydrogenation over Pt/Al_2O_3 in 2-pentanol

Pressure (MPa)	Initial hydrogenation rate (mmol/min/g_{Pt})			
	Temperature (K)			
	298	323	343	373
2.0	22.4	47.0	30.5	7.4
4.1	22.4	74.6	64.5	18.7

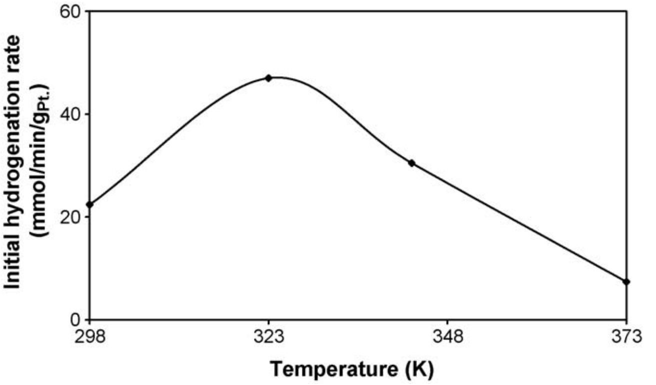

Fig. 3. The initial hydrogenation rates in citral hydrogenation in 2-pentanol at 2.0 MPa as a function of temperature.

time (Table 2). The initial hydrogenation rates as a function of temperature did not follow Arrhenius law, but instead exhibited a maximum as a function of temperature (Fig. 3). This maximum was achieved at 323 K under 2.0 MPa corresponding to the value of 47 mmol/g_{Pt}/min. This result indicated that lower initial rates were obtained above the maximum temperature due to catalyst deactivation. The reason for catalyst deactivation is most probably blocking of the active sites due to decarbonylation of unsaturated alcohols (see Section 3.2.3). Qualitatively the results at 2.0 and 4.1 MPa are very similar. Therefore for the sake of clarity the following treatment is mainly limited to data obtained at 2.0 MPa.

3.2.2.2. Effect of temperature on conversions after prolonged reaction times. The conversions after prolonged time could be compared at $\rho_{bulk} \times$ time of 200 mmol/g_{cat} min (Table 3). An unusual, not well-defined minimum in conversion was observed. This minimum conversion occurred at 343 K being only 65% from the level observed at 298 K (Table 3). This minimum conversion as a function of reaction temperature can be explained with the catalyst deactivation caused by decarbonylation, which has two different opposite trends occurring on the catalyst surface simultaneously with increasing temperature, i.e. increasing rate for decarbonylation reaction versus the enhanced desorption of CO from the catalyst surface.

Table 3
The conversions at $\rho_{bulk} \times \text{time} = 200\ g/dm^3$ min in citral hydrogenation over Pt/Al_2O_3 in 2-pentanol

Pressure (MPa)	Conversion (%)			
	Temperature (K)			
	298	323	343	373
2.0	89	78	58	60
4.1	98	85	68	74

The ratio of *trans* and *cis* isomers of citral during citral hydrogenation was compared as a function of temperature and $\rho_{bulk} \times$ time. The amount of *cis* citral was nearly independent on temperature, but increased with increasing $\rho_{bulk} \times$ time indicating that under the reaction conditions causing more severe catalyst deactivation the *trans* citral reacted more slowly. Moreover, *trans* citral is more stable at higher temperatures. It is, however, difficult to exclude the possibility that the isomerisation of *cis* citral to *trans* citral occurred under the reaction conditions. Analogously to the current results *trans* to *cis* citral ratio decreased with increasing conversion in citral hydrogenation in hexane 373 K at 0.5 MPa over Pt/active carbon catalyst, when also catalyst deactivation was observed [12].

3.2.2.3. Effect of temperature and pressures on product distribution. The main products in citral hydrogenation in 2-pentanol over Pt/Al_2O_3 catalyst in the temperature range of 298–373 K, were citronellal, nerol and geraniol, 3,7-dimethyloctanal and citronellol (Figs. 4–8 and Table 4). The amounts of 3,7-dimethyloctanol were maximally below 4% at 298 K. Only traces of isopulegol were formed, opposite to the results of Singh and Vannice [3], where citral hydrogenation was investigated over Pt/SiO_2 catalyst in hexane leading to maximally 5% isopulegol.

The parallel formation of the first primary products, an aldehyde, citronellal and unsaturated alcohols, nerol and geraniol was observed with the ratio between the initial concentrations for citronellal and nerol and geraniol ranging from 15 to 2 (decreasing with temperature increase). Enhanced formation of unsaturated alcohols as higher temperatures is correlating well with the results obtained in citral hydrogenation over Pt/SiO_2 catalyst [3]. It has been reported that the bond dissociation energies and heats of adsorption of C=C and C=O bonds are different and the dissociation energy for the latter bond being 7.9 kJ/mol larger than that for C=C [15]. Furthermore, the distribution between

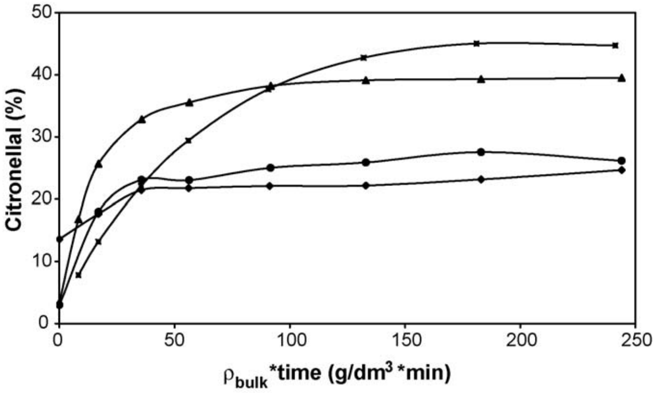

Fig. 4. Formation of citronellal as a function of $\rho_{bulk} \times$ time at 2.0 MPa at: (■) 298 K, (▲) 323 K, (●) 343 K and (♦) 373 K under 20 bar total pressure in 2-pentanol over Pt/Al_2O_3 catalyst.

Table 4
Kinetic data for citral hydrogenation over Pt/Al_2O_3 in 2-pentanol at 20 bar

Temperature (K)	*trans*/*cis* citral ratio	n + g (mol%)	cal (mol%)	dnal (mol%)	col (mol%)	dmol (mol%)
298	0.74	2	45	20	9	3
323	0.74	7	39	9	13	2
343	0.86	14	27	2	10	<1
373	0.91	24	23	<1	9	3[a]

Values are given at $\rho_{bulk} \times \text{time} = 200\,g/dm^3$ min. Abbreviations: n, nerol; g, geraniol; cal, citronellal; col, citronellol; dnal, 3,7-dimethyloctanal; dmol, 3,7-dimethyloctanol.

[a] Formed initially during the heating period.

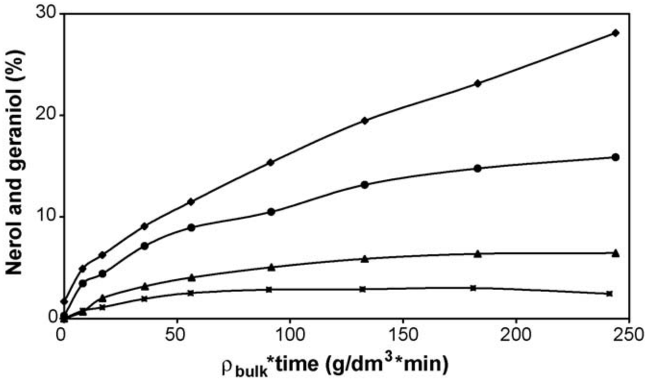

Fig. 5. Formation of nerol and geraniol as a function of ρ_{bulk} × time at 2.0 MPa at: (■) 298 K, (▲) 323 K, (●) 343 K and (♦) 373 K in 2-pentanol over Pt/Al_2O_3 catalyst.

citronellal and nerol and geraniol is most probable not affected by the isomerization of unsaturated alcohols nerol and geraniol to citronellal, since that reaction did not occur over Pt/SiO_2 catalyst [3].

After prolonged reaction times the formed amounts of citronellal decreased monotonically with increasing temperature at 2.0 MPa (Fig. 4 and Table 4) opposite to the formed amounts of nerol and geraniol (Fig. 5 and Table 4).

The ratio between geraniol and nerol is given at ρ_{bulk} × time of 50 mmol/min g_{cat} in Table 5. The formation of a *trans* isomer, geraniol, was enhanced at higher temperatures giving the ratio

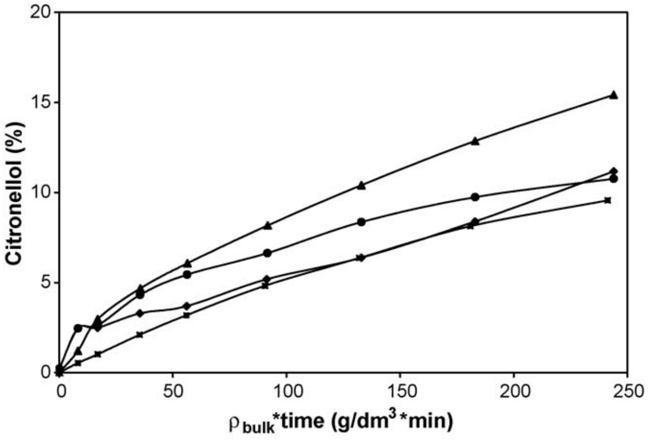

Fig. 6. Formation of citronellol as a function of ρ_{bulk} × time at 2.0 MPa at: (■) 298 K, (▲) 323 K, (●) 343 K and (♦) 373 K in 2-pentanol over Pt/Al_2O_3 catalyst.

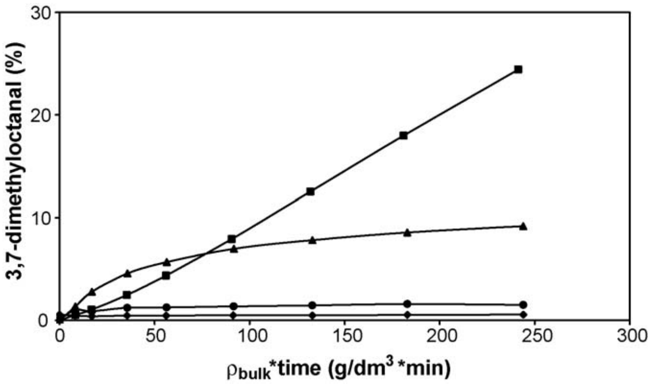

Fig. 7. Formation of 3,7-dimethyloctanal as a function of ρ_{bulk} × time at 2.0 MPa at: (■) 298 K, (▲) 323 K, (●) 343 K and (♦) 373 K in 2-pentanol over Pt/Al_2O_3 catalyst.

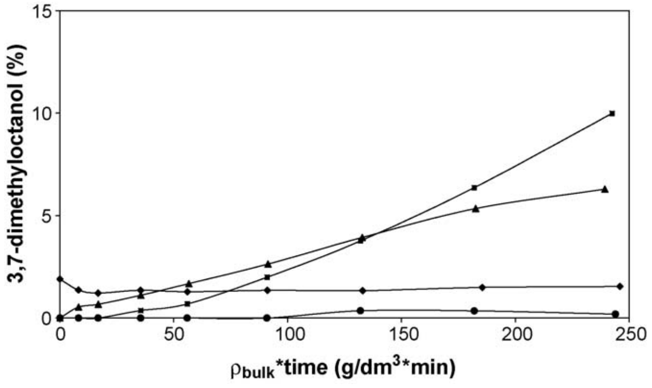

Fig. 8. Formation of 3,7-dimethyloctanol as a function of ρ_{bulk} × time at 2.0 MPa at: (■) 298 K, (▲) 323 K, (●) 343 K and (♦) 373 K in 2-pentanol over Pt/Al_2O_3 catalyst.

Table 5
Kinetic data from citral hydrogenation over Pt/Al_2O_3 in 2-pentanol at 2.0 MPa as a function of temperature

Entry	298 K	323 K	343 K	373 K
1	1.4	1.3	1.8	1.8
2	1.0	0.9	2.4	5.2
3	14.5	13.9	13.4	6.5

Entries: (1) the geraniol to nerol ratio at $\rho_{bulk} \times \text{time} = 50\,g/dm^3$ min, (2) the ratio between the initial formation rates of citronellal and 3,7-dimethyloctanal and (3) the ratio between the initial formation rates of citronellal and citronellol.

geraniol to nerol about 1.8. This value is in accordance with the results of Aumo et al. [16], where the ratio was about 2 over Pt/C catalyst at 373 K and 0.5 MPa. The effect of pressure on the geraniol-to-nerol ratio was quite minor. At higher temperatures, however, the formation of geraniol was slightly favored at lower pressures, since the hydrogenation rates were lower under these conditions, which in turn enhances isomerisation.

Citronellal reacted further to citronellol and 3,7-dimethyloctanal. The ratio between the initial formation rates for citronellol and 3,7-dimethyloctanal is presented in Table 5. The largest value for this ratio was obtained at 373 K, i.e. under the conditions, were catalyst deactivation was most prominent leading to very low levels for 3,7-dimethyloctanal. Under other reaction conditions this ratio is maximally 1.0 and it increased with increasing temperature indicating that the hydrogenation of a carbonyl bond is dramatically enhanced at 373 K compared to the hydrogenation of an isolated ethylenic double bond at C8 in citronellal. This result is agreeing well with the reaction thermodynamics in the hydrogenation of either C=C or C=O bond, i.e. the hydrogenation of the latter bond is enhanced at higher temperatures [3]. The highest selectivity to citronellol was 18% at 323 K. The lower selectivity at higher temperatures is caused by the catalyst deactivation inhibiting the further hydrogenation of citronellal. Similar conclusions follow from the analysis of 3,7-dimethyloctanol formation.

3.2.3. *Catalyst deactivation*

The catalyst deactivation was more prominent in cyclohexane than in 2-pentanol as mentioned above. The origin for the more severe catalyst deactivation in cyclohexane is coking, since the specific surface area of a spent catalyst used in citral hydrogenation at 373 K in cyclohexane was 56 m^2/g_{cat}, i.e. 41% of the specific surface area of the fresh catalyst. On the other hand only 15% decrease in the specific surface area, i.e. 81 m^2/g_{cat}, was observed in the spent catalyst in 2-pentanol. Additionally the micropores were blocked more when the catalyst was more deactivated. Analogous results were observed previously in citral hydrogenation over Ni/SiO_2 fibrous catalyst [7].

Desorption of carbonaceous species from the spent catalyst surface was investigated by temperature programmed desorption technique. Two catalysts, used either at 298 or 343 K under 2.0 MPa in 2-pentanol were studied. Three different gases, CO_2, CO and CH_4, were desorbed during TPD measurements under helium as a carrier gas (Fig. 9 and Table 6). The formation of ethene ($m/z = 28$) can be excluded, since it should decompose in the mass spectrometry giving simultaneously peak at $m/z = 14$, which was, however, absent. For the spent catalysts the desorbing gases confirmed the presence of carbonaceous species on the surfaces of these catalysts.

The relative peak areas of the desorbing gases for two different spent catalysts are given in Table 6. When the catalyst was used either at 343 or at 298 K at 2.0 MPa hydrogen in 2-pentanol, the relative amounts of CO_2, CO and CH_4 decreased indicating that there was more carbonaceous species on the catalyst surface used at 343 K than at 298 K. The main part of the desorbed gases in both the spent catalysts was CO, whereas the parts of CO_2 and CH_4 were less than 22% from the peak areas of CO. About 80% of CO desorbed above 690 K with a maximum desorption between 623 and 632 K from a spent catalyst used at 343 K (Fig. 9 and Table 6) indicating that the formed CO is very strongly bound on the catalyst surface.

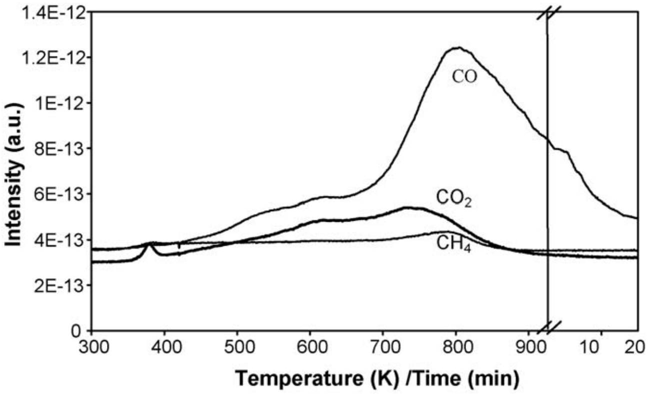

Fig. 9. TPD under helium from a spent catalyst used in citral hydrogenation in 2-pentanol under 298 K and 2.0 MPa.

The origin for the catalyst deactivation during citral hydrogenation was elucidated in this work by two additional experiments. Both citral and geraniol TPD experiments were carried out over a fresh, reduced Pt/Al_2O_3 catalyst. There was a difference in results between these two experiments, namely CO was formed in the latter case, whereas no CO was detected during citral TPD (figures are not presented). The maximum amount of CO desorbed was achieved between 833 and 903 K indicating that the CO is strongly bound to the catalyst surface. This result suggests that especially unsaturated alcohols are active for decarbonylation. The absence of CO formation in citral TPD is, however, somewhat unexpected result, since decarbonylation of shorter chain molecules, i.e. acrolein and crotonaldehyde occurred on Pt(1 1 1) surfaces during TPD experiment carried out in vacuum [17,18]. On the other hand TPD for these molecules was performed in conditions very remote from ones in the present work. Decarbonylation reaction has been generally accepted to occur during the hydrogenation of unsaturated aldehydes. It has been stated that especially unsaturated alcohols are active for decarbonylation. When CO is blocking the active sites on the catalyst surface, the CO coverage is determined at a certain temperature by two factors: desorption of CO and formation of CO most probable via decarbonylation of

Table 6
TPD of spent Pt/Al_2O_3 catalysts

Catalyst	Product	$T_{max, I}$ (K)	$T_{max, II}$ (K)	Total relative peak area
Used at 343 K, 2.0 MPa	CO_2	451	413–516	0.22
	CO	705–740	623–632	1.0
	CH_4	453–873	–	0.06
Used at 298 K, 2.0 MPa	CO_2	381	729–753	0.08
	CO	613–645	753–767	0.85
	CH_4	377–800	–	0.03

The amounts of the desorbed CO_2, CO and CH_4 and the temperatures for the maximum amount of desorption from two different spent catalysts in citral hydrogenation in 2-pentanol.

Table 7
TPO of spent Pt/Al_2O_3 catalysts

Catalyst	Product	Relative area of peak I	$T_{max, I}$ (K)	Relative area of peak II	$T_{max, II}$ (K)	Total relative peak area
Used at 343 K, 2.0 MPa	CO_2	0.69	418	0.31	509–531	1.0
	CO	0.03	415–427	–	–	0.03
	CH_4	0.04	413–425	–	–	0.04
Used at 298 K, 2.0 MPa	CO_2	0.63	399	0.22	484–492	0.85
	CO	0.01	388–405	–	–	0.01
	CH_4	0.02	393–408	–	–	0.02

The amounts of the desorbed CO_2, CO and CH_4 and the temperatures for the maximum amount of desorption from two different spent catalysts in citral hydrogenation in 2-pentanol.

unsaturated alcohols, nerol and geraniol. Both these phenomena, which affect the amount of CO in opposite directions, are enhanced with increasing temperature. Analogous considerations about the effect of temperature on the catalyst performance were presented in ref. [3]. Moreover, in geraniol and nerol hydrogenation over Pt/SiO_2 fast catalyst deactivation occurred at 373 K under 2.0 MPa in hexane [18] as well as in the hydrogenation of nerol over Rh/Al_2O_3 at 363 K in 2-pentanol [2]. Furthermore, in competitive hydrogenation of citronellal and geraniol the conversion of the former reactant was retarded, whereas when hydrogenating it alone under analogous conditions no significant loss of catalytic activity was observed [19]. In citral hydrogenation over Pd/Al_2O_3 CO evolution was confirmed by in situ ATR-IR techniques [19]. There exist spectroscopic evidences for the formation of CO in the hydrogenation of unsaturated aldehydes over Pt catalysts [11]; CO desorption was observed from Pt(1 1 1) surface exhibiting an activation barrier of 6.2 kJ/mol [20,21].

The spent catalysts were additionally analyzed by temperature programmed oxidation (Table 7). The main desorbing product from temperature programmed oxidation experiments of spent catalysts was CO_2 with $m/z = 44$, whereas CO and CH_4 corresponding to the m/z values of 28 and 16, respectively, were in minor amounts (Fig. 10 and Table 7). Interestingly it can be noticed that the total peak areas obtained in TPO were two orders of magnitude larger than those areas obtained during TPD and thus it is impossible to regenerate the catalyst by heat treatment under helium. Two different catalysts, i.e. either used in citral hydrogenation in 2-pentanol at 343 or at 298 K under 2.0 MPa were compared with TPO techniques. From the latter sample the total relative peak area for desorbed CO_2 was 85% of the former one indicating that more carbonaceous species was accumulated on the catalyst used at 343 K. The TPO from the catalyst used at 343 K in citral hydrogenation consists of two maxima for the CO_2 desorption. The first peak exhibiting the maximum at 418 K contained 69% of the total relative amount of CO_2 (Table 7), whereas the corresponding peak in the catalyst used at 298 K had the maximum for CO_2 desorption at 399 K, i.e. at 19 K lower temperature than the former one. An analogous trend was visible in the second peak indicating that formed CO_2 was less strongly bound on the Pt/Al_2O_3 catalyst spent at 298 K compared to the catalyst used at 343 K. The temperatures for the maximum desorption of CH_4 and CO were lower for the catalyst used at 298 K than at 343 K. It can be concluded that larger amounts of carbon containing species were adsorbed on the spent catalyst used at 343 K than at 298 K and these species were more strongly adsorbed on the former catalyst than on the latter catalyst, since higher temperatures for maximum amount of desorbed species were recorded for the latter catalyst. This result can partially explain the inverse relationship between the conversion levels and the reaction temperature.

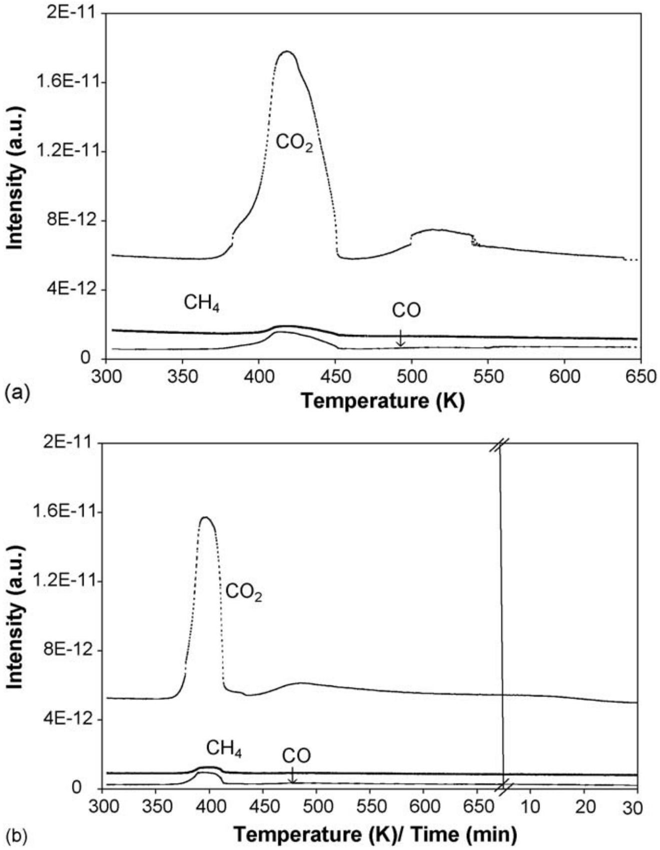

Fig. 10. Temperature programmed oxidation from the spent catalyst: (a) used at 298 K and (b) at 343 K at 2.0 MPa in 2-pentanol in citral hydrogenation.

4. Conclusions

Citral hydrogenation kinetics was studied in a batch reactor operating with an increasing catalyst amount with increasing time, which is an efficient way of studying consecutive reactions.

The initial hydrogenation rates showed a maximum as a function of temperature. It is concluded that due to catalyst deactivation the initial hydrogenation rates were lower at higher temperatures. The catalyst deactivation was confirmed by formation of CO during temperature programmed desorption from the spent catalyst. The specific surface areas dropped by maximally 41% compared to the fresh catalyst.

The conversions after prolonged reaction times showed a minimum as a function of temperature at 343 K. This minimum is a result of increased decarbonylation of unsaturated alcohols, nerol and geraniol as well as increased desorption of CO with increasing temperature.

The further hydrogenation of citronellal was decreased very much due to catalyst deactivation, whereas formation of nerol and geraniol was enhanced at higher temperatures.

Temperature programmed desorption of citral and geraniol from a reduced fresh catalyst confirmed that decarbonylation of an unsaturated alcohol, geraniol, occurred on the reduced Pt/Al_2O_3 surface, whereas no decarbonylation was observed during the temperature programmed desorption of citral over this catalyst.

Temperature programmed techniques, desorption and oxidation as well as nitrogen adsorption were used for analyzing the spent catalysts. In cyclohexane the specific surface area decreased more than in 2-pentanol. Moreover, the relative amount of large pores had increased compared to the fresh catalyst indicating blocking of the micropores. Temperature programmed desorption confirmed the existence of carbonaceous species on the surface of the spent catalysts. Methane, CO and CO_2 were formed during temperature programmed desorption experiments. With reaction temperature increase higher amounts of more strongly adsorbed species were formed. Their presence on the catalyst surface during citral hydrogenation is responsible for unconventional temperature dependence, i.e. negative apparent activation energy.

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