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Studies on partial hydrogenation of 1,5,9-cyclo-dodecatriene towards cyclo-dodecene

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Dedicated to Herbert Vogel on the occasion of his 60th birthday.

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ABSTRACT

The selective hydrogenation of 1,5,9-*cis*,*trans*,*trans*-cyclo-dodecatriene (1,5,9-*ctt*-CDT) towards cyclo-dodecene (CDE) depends strongly on the pressure of hydrogen, respectively the hydrogenation rate. High yields of CDE (>90%) can only be reached at extremely low hydrogen pressure. In order to elucidate this exceptional reaction performance the course of reaction has been studied for a wide range of hydrogen pressure, $0.01 > p_{H_2} > 2.5$ MPa, taking into consideration data of other research groups. The CDT hydrogenations were discontinuously carried out in liquid phase on Pd/Al_2O_3 at $T = 353$ K.

The resulting hypothesis of this study is that the very low reaction rate at low p_{H_2} is necessary in order to realize a dense surface coverage of 1,5,9-CDT and 1,5-cyclo-dodecadiene (CDD) isomers where these molecules show adsorption on Pd via two double bonds so that readsorption of formed CDE and subsequent hydrogenation to cyclo-dodecane (CDA) is hardly possible.

On the whole this new hypothesis on the reaction course of CDT hydrogenation gives a sound and fully consistent view on this rather complicated reaction.

1. Introduction

Starting material of the synthesis of laurolactam the monomer for the production of Nylon-12 is 1,5,9-*ctt*-cyclo-dodecatriene which is obtained by catalytic cyclo-trimerisation of butadiene. The usual synthetic route proceeds via oxidation of cyclo-dodecane (CDA) to cyclo-dodecanone which is unsatisfactory with respect to selectivity.

The route via the selective hydrogenation of CDT towards CDE is a promising alternative, Fig. 1. CDE could be oxidised with H_2O_2 to the epoxide which can be catalytically transformed into cyclo-dodecanone as proposed by Wilke [1]. CDE can also be oxidised with N_2O to cyclo-dodecanone as recently patented by BASF [2]. Furthermore CDE can serve as starting material for the production of 1,10-decane dicarboxylic acid.

In a group of studies CDT hydrogenations have been carried out under low hydrogen pressures achieving rather high CDE yields.

McAlister reported a CDE yield of 90% obtained in a liquid phase batch hydrogenation procedure applying a powdered catalyst of 5% Pd on charcoal at stepwise reduced hydrogen pressure between 0.2 and 0.025 MPa [3]. Wießmeier and Hönicke [4] and Herwig et al. [5] could also reach CDE yields of about 90% by continuous gas phase hydrogenation of CDT with Pd supported on alumina at rather low hydrogen pressures. Such high yields could also be obtained in a liquid phase batch procedure with Pd supported on alumina at stepwise reduced hydrogen pressure of 0.15 down to 0.007 MPa by Gaube et al. [6].

Another group of studies have been carried out under elevated p_{H_2} with the result of a markedly lower CDE yield.

For the liquid phase hydrogenation of CDT using a Pd/Al_2O_3 catalyst in a slurry reactor Stüber et al. [7] and Julcour et al. [8] observed an increasing CDE yield with decreasing hydrogen pressure. Benaissa et al. [9] extended these studies by detailed isomer analysis at hydrogen pressures in the range of 0.15–1.2 MPa. At 1.5 MPa a CDE yield of 74% was attained.

In a more detailed study of Zieverink [10] the dependences on hydrogen pressure are given for all analysed isomers, *c*,*c*,*t*-, *c*,*t*,*t*-, *t*,*t*,*t*-CDT; *c*,*c*-, *c*,*t*-, *t*,*t*-CDD; *c*-,*t*-CDE, for p_{H_2} between 0.33 and 2.5 MPa. The results show also an increasing CDE yield with decreasing p_{H_2}. At $p_{H_2} = 0.33$ MPa a CDE yield of 68% was attained. These data are reasonably represented by a model based on the reaction scheme, Fig. 2, taken from preceding works [11,12]. The increasing CDE yield with decreasing p_{H_2} has been formally described by an additional direct hydrogenation of CDD isomers towards CDE which was characterised by a second order in hydrogen.

Despite the knowledge of increasing CDE yield with decreasing p_{H_2} the experiments of Benaissa et al. and of Zieverink were not extended to lower p_{H_2} Therefore, the aim of the present work

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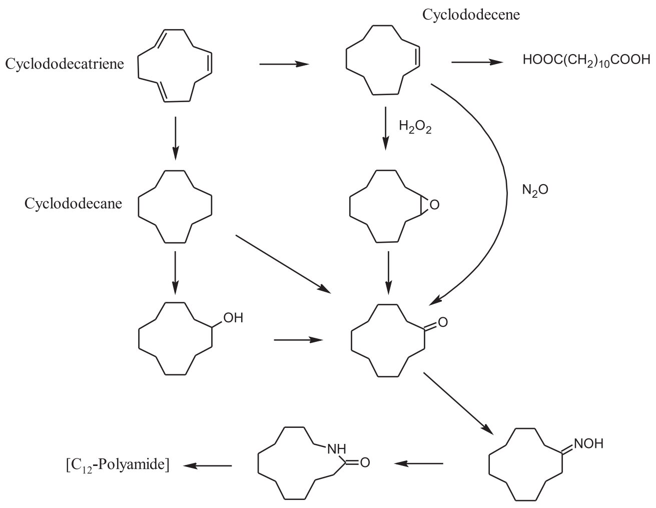


Fig. 1. Synthesis of laurolactam and of HOOC–$(CH_2)_{10}$–COOH.

is to study and interpret the influence of hydrogen pressure on the interdependence of isomerisation and hydrogenation and in particular on the CDE yield covering the range $0.007 < p_{H_2} < 2.5$ MPa by experiments of the present study and for $p_{H_2} \geq 0.33$ MPa by experiments of Zieverink.

2. Experimental

The experiments of the present study were carried out in a batchwise operated recycle reactor, Fig. 3.

The circulated liquid mixture of reactants (0.196 mol/l in n-decane) is saturated with hydrogen enhanced by a stirrer (about 500 rpm) to intensify the contact of gas and liquid. In equilibrium the concentration of hydrogen in n-decane is $c_{H_2} = 0.045\ p_{H_2}/\text{MPa}$ mol/l at 353 K. This liquid flows through a sieve in order to avoid entering of gas bubbles into the catalyst layer of egg-shell type Pd catalyst. The flow rate is kept high so that only a very small part of hydrogen is consumed during one passage through the catalyst layer, thus the concentration of reactants is nearly constant along the catalyst layer. The experiment is started by quick dosing of CDT using a syringe.

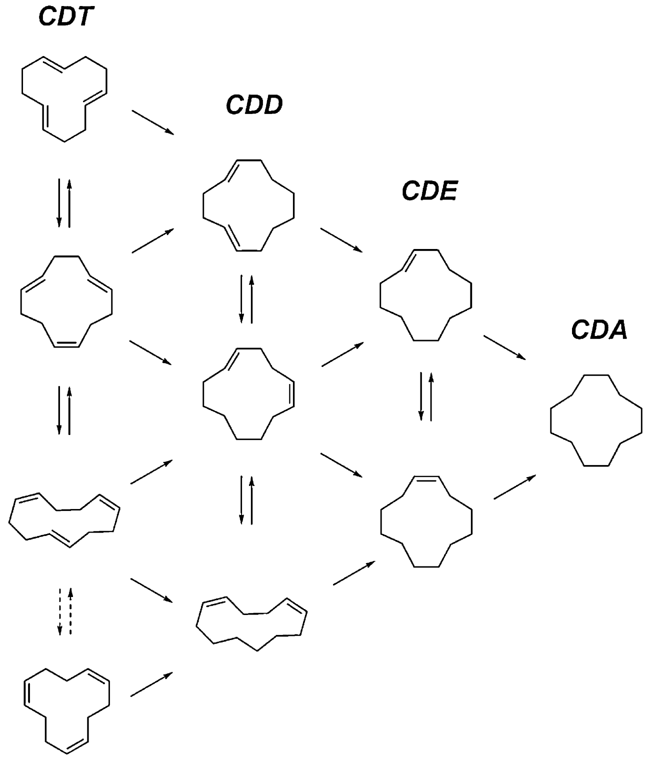


Fig. 2. Reaction scheme of 1,5,9-CDT hydrogenation.

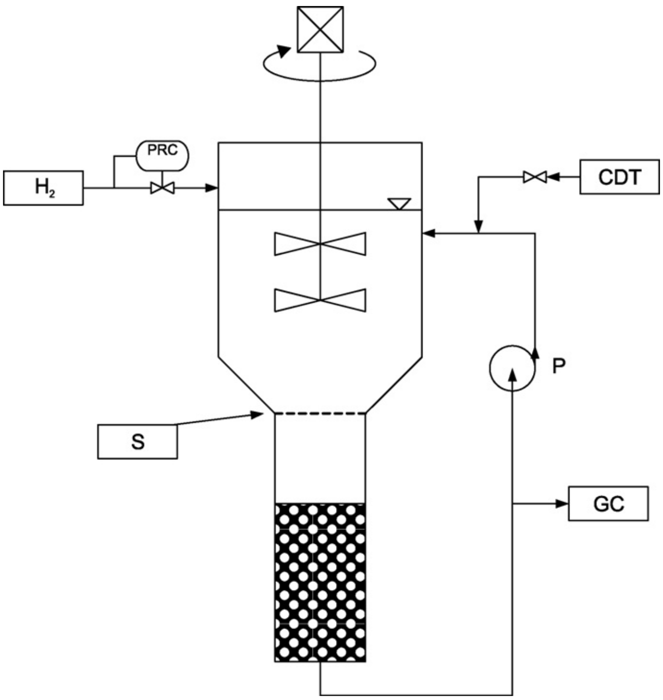


Fig. 3. Experimental unit of liquid phase hydrogenation. P, circulation pump; S, sieve; GC, gas chromatograph.

The hydrogenation of 1,5,9-*ctt*-CDT has been studied at different hydrogen pressures and for stepwise reduced hydrogen pressures. For elucidation of the reaction course also the hydrogenation of the intermediate product 1,5,9-*ttt*-CDT was carried out.

For all experiments of the present study a catalyst of egg-shell type was used. The properties of this catalyst are listed in Table 1. For all experiments carried out with this catalyst an influence of mass transfer on the course of reaction could be excluded [6].

The discontinuous hydrogenation of CDT and CDD needs several hours while the time required for a 90%-approach of steady state concentration within the active layer of the catalyst is about 20 s. Therefore, the concentration profiles in the active layer of the catalyst pellets are in quasi steady state because of the very slow change of concentrations in the surrounding liquid.

In order to extend the pressure range of hydrogenation experiments for theoretical discussion we used the experimental work of

Table 1
Structural properties of the catalyst.

Diameter of pellets [mm]	2–3
Thickness of active layer [μm]	20
BET surface [m^2/g]	108
Porosity %	67
Pore volume > 7.6 nm [cm^3/g]	0.52
Pore volume < 7.6 nm [cm^3/g]	0.06
Maximum of pore distr. [nm]	6–7
Pd content wt%	0.1
Pd surface [m^2/g]	0.05–0.1
Degree of dispersion %	18
Pd particle size [nm]	2–3

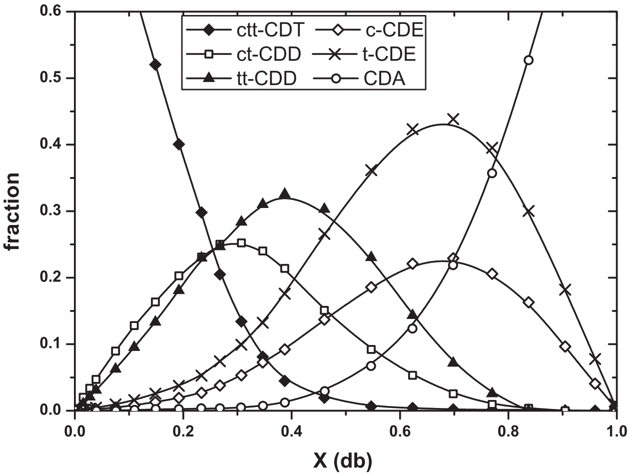


Fig. 4. Experiment 1. Product composition of 1,5,9-*ctt*-CDT hydrogenation. 3.75 g catalyst, $p_{H_2} = 0.15$ MPa, $n_{CDT} = 0.0274$ mol, $c_{CDT} = 0.196$ mol/l, $T = 353$ K.

Zieverink [10]. Together with our study this dependence on p_{H_2} can now be discussed for the wider range between 0.007 and 2.5 MPa.

Zieverink employed a stirred batch autoclave filled with the slurry of powdered Pd/alumina in CDT diluted with n-decane at a concentration of 0.35 mol/l. Just as for our experiments it could be proved that mass transfer does not affect the conversion so that all results used in our study represent true kinetics. Product analysis has been carried out by gas chromatography using a silica capillary: $L = 30$ m, $d_{int.} = 0.25$ mm coated with 0.25 μm DB-wax. It should be noted that the identification of compounds in the gas chromatogram of our study is in agreement with that of Zieverink [10].

In order to study the interdependence of isomerisation and hydrogenation batchwise liquid phase and continuously operated gas phase experiments with *c*-2-butene as model reaction were carried out. The experimental unit for the latter is described by Wuchter [13].

3. Results

Figs. 4–6 show the results of *ctt*-CDT conversions. The hydrogenation rate of experiment 1 (maximum CDE yield 0.68) is 3.78 mol (H_2)/h g(Pd), constant up to 55% double bond conversion.

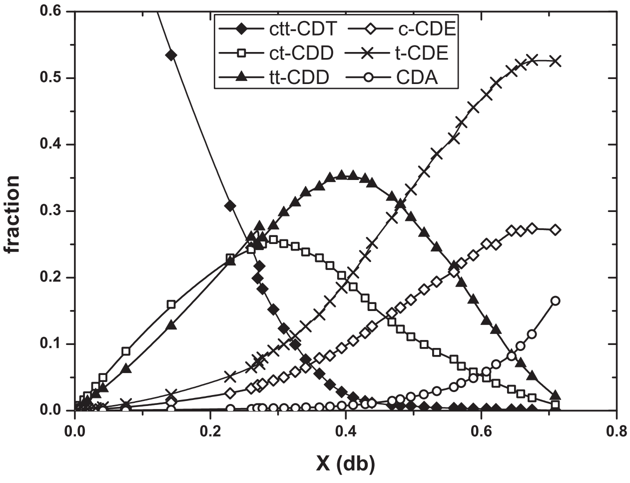


Fig. 5. Experiment 2. Product composition of 1,5,9-*ctt*-CDT hydrogenation. 4.76 g catalyst, $n_{CDT} = 0.0274$ mol, $c_{CDT} = 0.196$ mol/l, $T = 353$ K, $p_{H_2} = 0.15$ MPa ($x_{db} = 0$–0.28), $p_{H_2} = 0.03$ MPa ($x_{db} = 0.28$–).

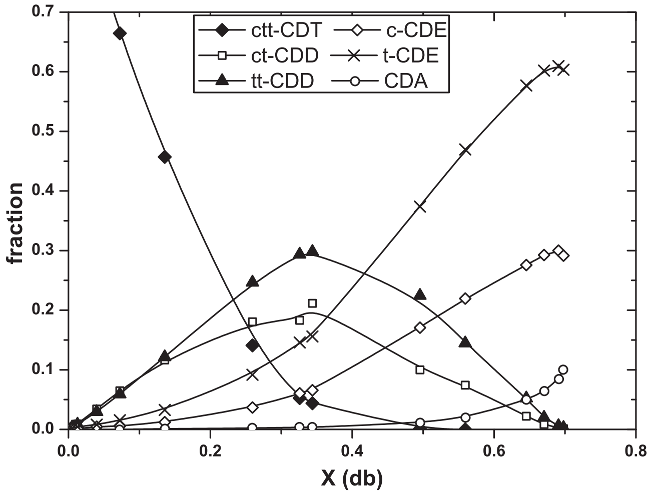


Fig. 6. Experiment 3. Product composition of 1,5,9-*ctt*-CDT hydrogenation. 4.8 g catalyst, $n_{CDT} = 0.0274$ mol, $c_{CDT} = 0.196$ mol/l, $T = 353$ K, $p_{H_2} = 0.05$ MPa ($x_{db} = 0$–0.35), $p_{H_2} = 0.025$ MPa ($x_{db} = 0.35$–0.65), $p_{H_2} = 0.007$ MPa ($x_{db} = 0.65$–).

For all experiments of the present study the hydrogenation is first order with respect to hydrogen [6].

The fractions are plotted versus the degree of double bond hydrogenation *x*(db) which is defined as $X_{db} = x_{db}^0 - x_{db}/x_{db}^0$ with x_{db} the fraction of double bonds.

$X_{db} = 1$ indicates complete hydrogenation of CDT.

Much higher CDE yields are obtained with further decreasing p_{H_2}. In order to avoid too long reaction times in our experiments the hydrogen pressure is reduced stepwise. Figs. 5 and 6 show the product composition of experiment 2 (maximum CDE yield 0.8), and experiment 3 (maximum CDE yield 0.9).

A further increase of CDE yield up to 0.93 was attained in the presence of CO as explained by Gaube et al. [6].

Fig. 7 shows an experiment of Zieverink under a hydrogen pressure of 0.8 MPa.

The experiment of Zieverink was carried out at $T = 433$ K, 80 K higher than for our experiments. However, following his study the influence of temperature is small so that a comparison with our data is justified.

In all these experiments *cct*-CDT and *cc*-CDD show fractions less than 0.03. The formation of the intermediate *ttt*-CDT strongly

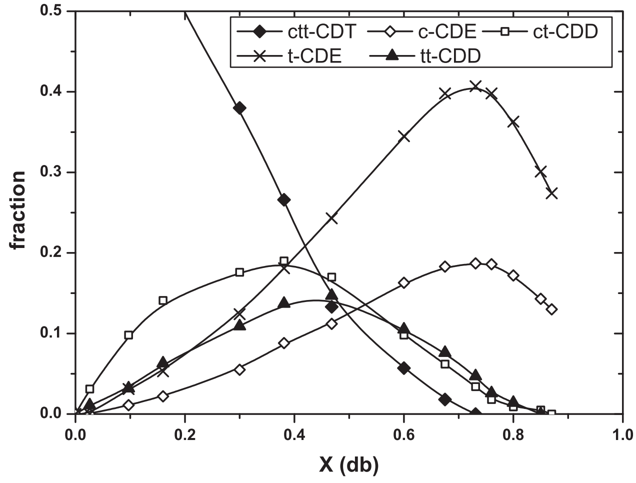


Fig. 7. 1,5,9-*ctt*-CDT hydrogenation by Zieverink [10]. $c_{CDT} = 0.35$ mol/l, $p_{H_2} = 0.8$ MPa, $T = 433$ K, *x*(db) is the degree of double bond hydrogenation.

Table 2
Maximum fraction of *ttt*-CDT.

	Fraction *ttt*-CDT	p_{H_2}/MPa
Zieverink	0.023	2.5
”	0.038	1.6
”	0.045	0.8
”	0.059	0.33
Experiment 1	0.107	0.15
Experiment 2	0.127	0.05

depends on p_{H_2} as shown by the maximum fraction listed in Table 2 including some further results of Zieverink.

For a better understanding of the reaction course the hydrogenation of *ttt*-CDT is presented in Fig. 8.

In the study of Zieverink [10], and in the present study positional isomers beside 1,5,9-CDT and 1,5-CDD show very small fractions and disappear already at moderate degree of conversion. Therefore, in the reaction scheme, Fig. 2, only *cis*/*trans* isomerisations are considered.

4. Discussion

4.1. Interdependence of isomerisation and hydrogenation

In order to give a better insight into the interrelation between hydrogenation and isomerisation experiments with *c*-2-butene as a model were carried out in both continuous gas phase and discontinuous liquid phase operation. Fig. 9 shows the reaction rates of hydrogenation and isomerisation of *c*-2-butene towards *t*-2-butene and to a minor extent of about 10% to 1-butene.

For the isomerisation this diagram reveals with respect to hydrogen a change from first order at very low hydrogen pressure up to zero order and finally to negative order at high hydrogen pressure. The hydrogenation towards butane is of first order with respect to hydrogen. This dependence of hydrogenation and isomerisation on hydrogen pressure could be well represented by a kinetic model based on the reaction scheme, Fig. 10, already proposed by Horiuti and Polanyi [14] and still widely accepted. This model is based on the assumption of a dissociative adsorption of hydrogen

$$r_1 = k_1 \cdot P_{1\text{-}C_4H_8}\Theta_H, \quad c\text{-}C_4H_8 \xrightarrow{+H} C_4H_9{}^*$$
$$r_2 = k_2[C_4H_9{}^*](1-\Theta_H), \quad C_4H_9{}^* \xrightarrow{-H} t\text{-}C_4H_8$$
$$r_3 = k_3[C_4H_9{}^*]\cdot\Theta_H, \quad C_4H_9{}^* \xrightarrow{+H} C_4H_{10}$$

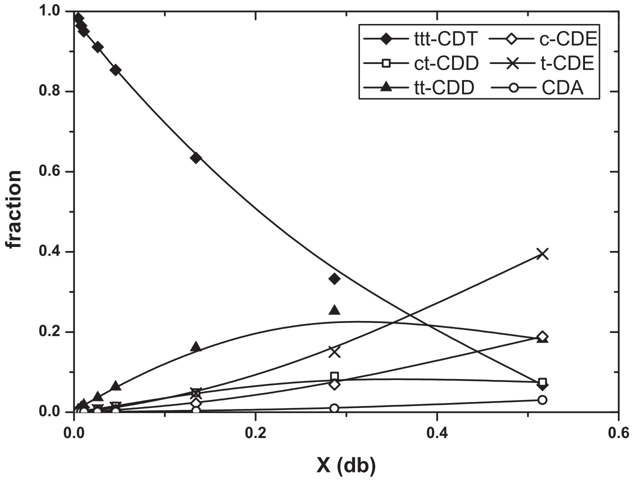


Fig. 8. Hydrogenation of 1,5,9-*ttt*-CDT. 4.8 g catalyst, $p_{H_2} = 0.1$ MPa, $n_{CDT} = 0.0274$ mol, $c_{CDT} = 0.196$ mol/l, $T = 393$ K.

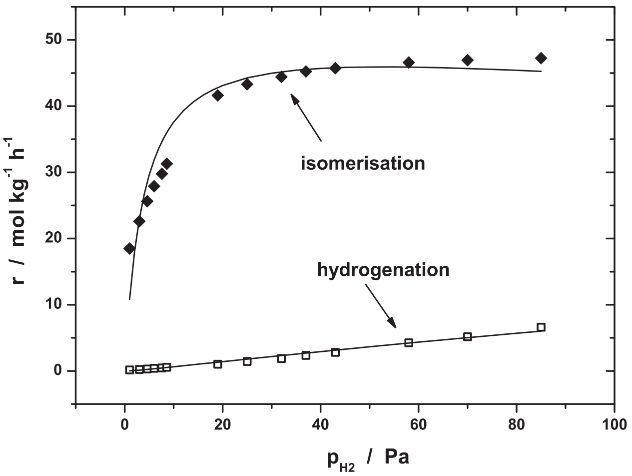


Fig. 9. Gas phase isomerisation and hydrogenation of *c*-2-butene towards *t*-2-butene and 1-butene (≈10%), $p_{c\text{-}2\text{-butene}} = 2000$ Pa, $T = 333$ K, $m_{cat} = 65$ mg (see Table 1).

Table 3
Liquid phase isomerisation and hydrogenation of *c*-2-butene. $T = 333$ K, 5.6 g *c*-2-butene in 65 g pentane, $m_{cat.} = 100$ mg.

p_{H_2}/MPa	*r* (isom.)/*r* (hydr.)
0.4	1.3
0.1	5.8
0.05	9.8

Θ_H denotes a formal measure of hydrogen availability. For modelling Θ_H is formally expressed by:

$$\Theta_H = \frac{K_H \cdot p_{H_2}}{1 + K_H \cdot p_{H_2}}$$

where K_H is a constant. [$C_4H_9{}^*$] symbolizes a formal surface coverage of this intermediate and can be eliminated by the steady state condition $r_1 = r_2 + r_3$.

The curves in Fig. 9 were generated with the parameters:

$$k_1/\text{mol kg}^{-1}\text{h}^{-1}\text{Pa}^{-1} = 0.0265, \quad \frac{k_3}{k_2} = 0.0054 \quad \text{and} \quad K_H/\text{Pa}^{-1} = 0.257$$

At very low p_{H_2} the rate determining step is assumed as the formation of the alkyl intermediate while with increasing p_{H_2} the abstraction of hydrogen is retarded by the decreasing number of hydrogen accepting sites.

For reaction conditions which are close to those of CDT hydrogenation Table 3 gives the ratios of isomerisation/hydrogenation for the conversion of *c*-2-butene in liquid phase at different hydrogen pressures. As for the gas phase reaction also the liquid phase procedure shows a strong increase of the isomerisation/hydrogenation ratio with decreasing hydrogen pressure.

Table 4 gives the ratio for the isomerisation/hydrogenation of *ctt*-CDT estimated from the diagrams listed in the table. The

Table 4
Liquid phase isomerisation and hydrogenation of *ctt*-CDT.

Experiment	p_{H_2}/MPa	*r* (isom.)/*r* (hydr.)
Zieverink [10], Fig. 7	0.8	0.98
Exp. 1, Fig. 4	0.15	1.92
Exp. 2, Fig. 5	0.15	1.88
Exp. 3, Fig. 6	0.05	3.93

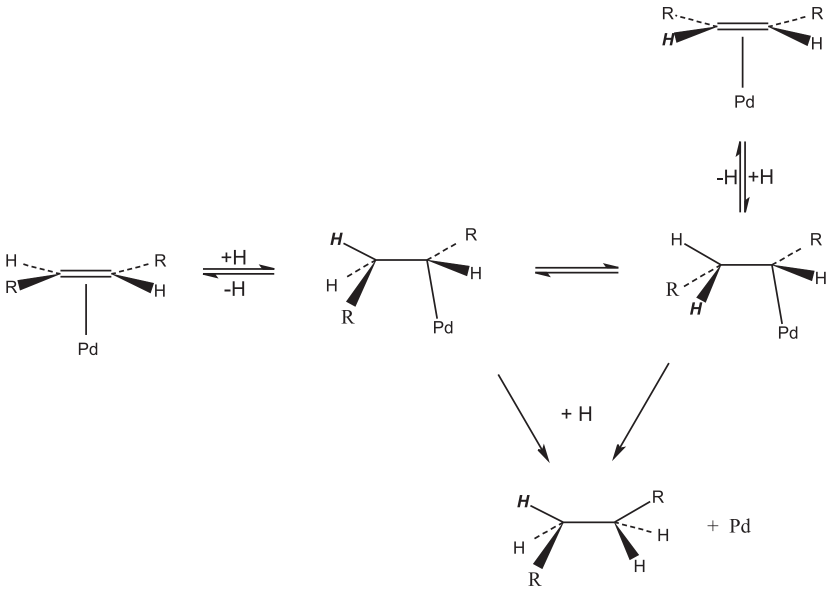


Fig. 10. Reaction scheme of hydrogenation/isomerisation (Horiuti and Polanyi).

dependence of this ratio on p_{H_2} is less strong than for *c*-2-butene which may be due to the lower mobility within the CDT ring.

Up to now the early reaction scheme proposed by Polanyi and Horiuti [14] is well accepted as a hypothesis. Starting with a π-coordinated alkene a semihydrogenation step leads to an alkyl which is bound to the Pd surface. The next steps are either the abstraction of hydrogen from β position of the alkyl forming again a π-coordinated alkene or the irreversible hydrogenation of the alkyl to alkane.

The abstracted hydrogen atom moves to a free site on Pd. If this abstraction happens after rotation in the alkyl group *cis*/*trans* isomerisation occurs.

The actions of hydrogen depend on the specific bonding of H atoms in different positions, on the surface, in the subsurface, and dissolved in the Pd lattice, Fig. 11 [15,16].

π-Coordinated alkene is prone to nucleophilic attack by surface hydride which generates a surface alkyl. Subsequent electrophilic attack at the α-C atom requires a positively charged H from the subsurface region.

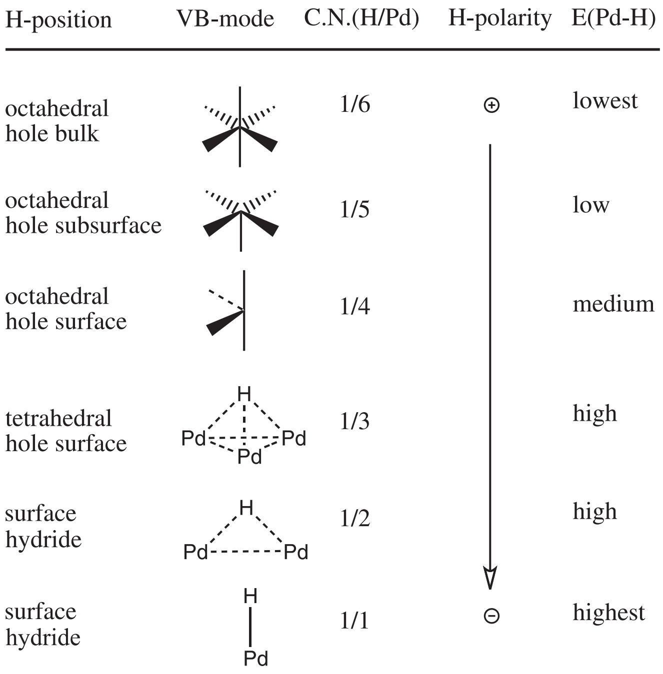
Many attempts have been made to identify intermediates in the hydrogenation of ethene as a model case by various spectroscopic methods as compiled in a review by Rupprechter [17]. However at room temperature no adsorbed species and intermediates could be identified by SFG spectroscopy for hydrogenations on Pd (1,1,1) [18] and model catalysts of Pd crystallites on Al_2O_3 support [19,20]. Nevertheless π-coordinated ethene is regarded as the reactive species.

4.2. Course of CDT hydrogenation

The diagrams of Zieverink, Fig. 7, and of the present study, Figs. 4 and 5, show a linear increase of *ct*-CDD formation and an s-shaped one of *tt*-CDD formation indicating the direct formation of *ct*-CDD by hydrogenation of *ctt*-CDT and the formation of *tt*-CDD by a consecutive reaction via *ttt*-CDT. The hydrogenation experiment of *ttt*-CDT, Fig. 8, is the direct proof of the formation of *tt*-CDD by hydrogenation of *ttt*-CDT. *ct*-CDD is formed by isomerisation of *tt*-CDD which must be assumed as a second route to *ct*-CDD in the conversion of *ctt*-CDT. The isomerisation of *ttt*-CDT to *ctt*-CDT is marginal due to the equilibrium in the group of 1,5,9-CDTs as already discussed by Zieverink [10].

In the modelling by Benaissa et al. [9] the isomerisation of *ctt*-CDT towards *cct*-CDT and its hydrogenation to ct-CDD appears as main reaction route while the direct hydrogenation of *ctt*-CDT is excluded. In general these authors assumed that *cis* double bonds are preferred in hydrogenation because of much stronger adsorption compared with *trans* double bonds.

The reason of this discrepancy between the interpretation of Benaissa et al. and that of Zieverink as well as ours could be clarified by a critical review of experimental data. In contrast to the data of Zieverink and of the present study the experiments of Benaissa et al. show for the formation of *cct*-CDT a very strong increase and after a short time a strong decrease which causes this wrong interpretation.



H-position	VB-mode	C.N.(H/Pd)	H-polarity	E(Pd-H)
octahedral hole bulk		1/6	⊕	lowest
octahedral hole subsurface		1/5		low
octahedral hole surface		1/4		medium
tetrahedral hole surface	H Pd Pd Pd	1/3		high
surface hydride	H Pd Pd	1/2		high
surface hydride	H Pd	1/1	⊖	highest

Fig. 11. Properties of hydrogen for different positions [15,16].

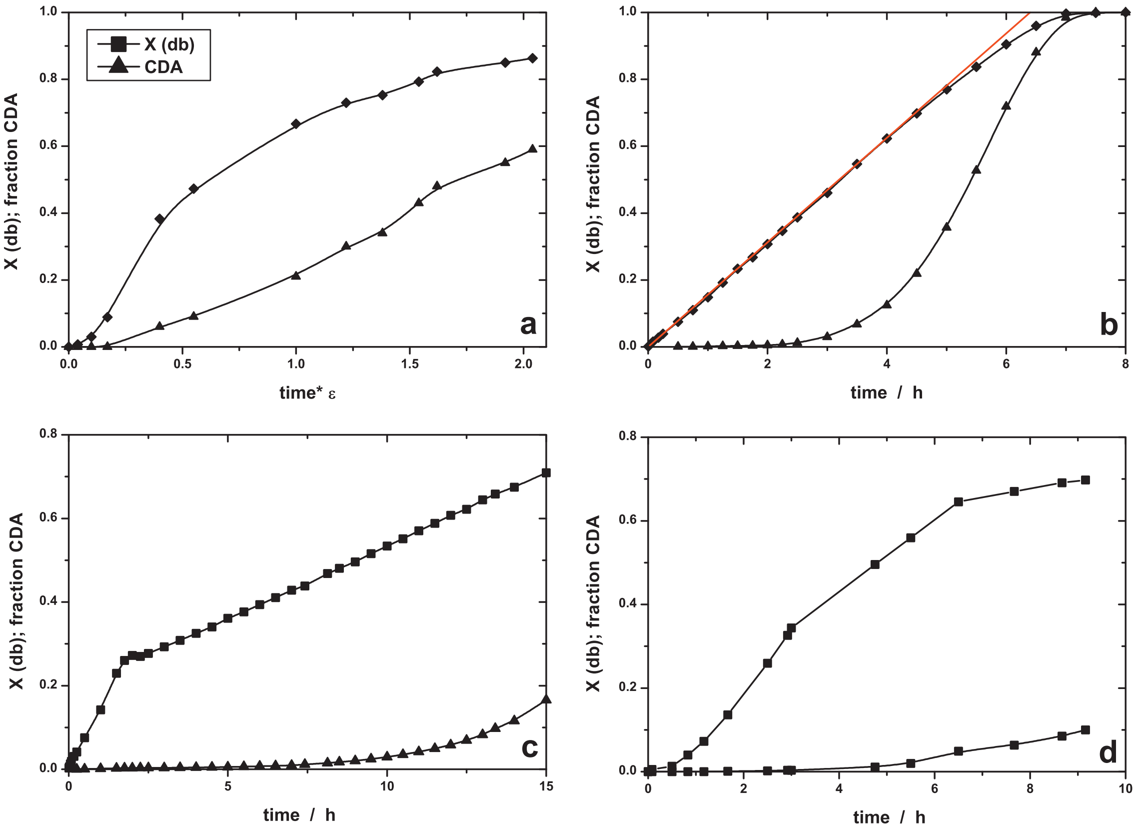


Fig. 12. Dependence of the degree of double bond hydrogenation and of CDA fraction on reaction time. (a) Experiment of Zieverink for $p_{H_2} = 0.8$ MPa [10], (b) Experiment 1, $p_{H_2} = 0.15$ MPa, (c) Experiment 2, $p_{H_2} = 0.03$ MPa ($x_{db} = 0.28$–), (d) Experiment 3, $p_{H_2} = 0.007$ MPa ($x_{db} = 0.65$–).

The results of Zieverink and of the present study show that the activity of hydrogenation of a double bond in *trans* conformation is similar or even preferred to that in a *cis* conformation of CDT in contradiction to the assumption of Benaissa et al. [9].

4.3. Dependence of selectivities on hydrogen pressure

The competition between isomerisation and hydrogenation is best demonstrated by the ratio of *tt*-CDD/*ct*-CDD formation. As with increasing p_{H_2} the ratio of hydrogenation and isomerisation increases experiments at high p_{H_2} as given in Fig. 7 show a ratio *ct*-CDD/*tt*-CDD >1 and at low p_{H_2} as given in Figs. 4–6 show a ratio < 1 because the formation of *ct*-CDD depends mainly on the hydrogenation of *ctt*-CDT while the first step of *tt*-CDD formation is the isomerisation of *ctt*-CDT to *ttt*-CDT. Table 2 shows that the maximum fraction of *ttt*-CDT increases with decreasing p_{H_2} due to the increasing ratio isomerisation/hydrogenation of *ctt*-CDT to *ttt*-CDT and to *ct*-CDD and due to decreasing hydrogenation of *ttt*-CDT to *tt*-CDD.

4.4. The effect of p_{H_2} on the CDE yield at very low p_{H_2}

The CDE yield obtained by Zieverink for $p_{H_2} = 0.8$ MPa is 0.63. Reduction of p_{H_2} leads to considerably increased CDE yields as shown for experiments 1–3, Figs. 4–6. The maximum CDE yields are:

$$0.68 \text{ at } p_{H_2} = 0.15\,\text{MPa}, \quad 0.80 \text{ at } p_{H_2} = 0.15\,\text{MPa}\,(x_{db} = 0\text{–}0.28), \quad p_{H_2}{=}0.03\,\text{MPa}\,(x_{db} = 0.28\text{–}), \quad 0.90 \text{ at } p_{H_2} = 0.05\,\text{MPa}\,(x_{db} = 0\text{–}0.35), \quad p_{H_2} = 0.025\,\text{MPa}\,(x_{db} = 0.35\text{–}0.65), \quad p_{H_2} = 0.007\,\text{MPa}\,(x_{db} = 0.65\text{–})$$

Zieverink has found that for $p_{H_2} \geq 0.33$ MPa the rate of hydrogenation follows first order in the concentration of double bonds. The plot x_{db}, degree of double bond hydrogenation, as function of time, Fig. 12a, shows the corresponding decrease of the slope with increasing time. This kinetic analysis has lead to the assumption that the surface of the catalyst is not densely covered by CDT/CDD [10]. Consequently, in this case CDE gets a chance of adsorption followed by consecutive hydrogenation towards CDA.

With decreasing p_{H_2} the first order in the concentration of double bonds changes towards zero order. For $p_{H_2} = 0.15$ MPa, Fig. 12b, strict zero order is observed in the range up to $x_{db} < 0.55$. Above this range the course of reaction approaches first order. For $p_{H_2} = 0.03$ in the range $x_{db} > 0.3$ the zero order is extended over the whole range, Fig. 12c. This is also demonstrated for experiment 3, Fig. 12d, at further reduced p_{H_2}. As demonstrated in these diagrams, Fig. 12a–d, the increase of the CDA fraction correlates with the deviation from zero order in the fraction of double bonds towards first order.

This leads to the assumption that the adsorption of CDE is prevented by densely adsorbed CDT and CDD isomers. The preference for CDT/CDD adsorption with respect to CDE adsorption is explained by the further assumption that CDT and CDD always utilise two double bonds for contact with the surface of the catalyst and thus are more strongly adsorbed than CDE following the early concept of Bond and co-workers as discussed for many other systems [21].

Therefore, we considered the adsorption of *tt*-, *ct*- and *cc*-1,5-CDD molecules on a Pd surface using standard molecular models as exemplified for *ct*-1,5-CDD in the graphical abstract. All isomers show a suitable conformation for contact with two double bonds.

Of course this mechanistic consideration lacks strict physical support. However, it is still very difficult to calculate the dynamic adsorption process of CDT or CDD molecules from a liquid on a Pd surface.

We assume that at very low p_{H_2} the surface is densely covered first with CDT and then with CDD isomers down to a low concentration of CDD. However, at high hydrogen pressure and consequently high hydrogenation rate this dense adsorption layer is not replenished fast enough and CDE gains an increasing chance of adsorption and hydrogenation towards CDA.The contact via two double bonds suggests that isomerisation and hydrogenation can simultaneously occur at both adsorbed double bonds. However, at the moment of hydrogenation of the double bond the very high reaction enthalpy can be assumed as concentrated on the molecule just formed. Dissipation of this energy may occur by collision with neighbouring molecules and also via the chemisorption bonds to the Pd lattice. Thus, vibrations perpendicular to the surface are strongly activated so that desorption of this molecule occurs [22]. This may be the reason that only one of the double bonds can be hydrogenated within the residence time of adsorption. Therefore, we expect and in all experiments find a strictly consecutive hydrogenation CDT → CDD → CDE → CDA. Therefore, the assumption of an additional direct hydrogenation of CDD to CDA by Zieverink is excluded. On the other hand isomerisations can occur at both adsorbed double bonds. This may be the reason that we find CDE formed by hydrogenation of CDD in the equilibrated *c*/*t* ratio of about ½ even in a range of reaction where readsorption of CDE can be excluded because its hydrogenation is negligible.

For modelling following our hypothesis an expression must be found which describes this complicated interdependence of CDT/CDD adsorption and readsorption of CDE as a function of p_{H_2}. However, for such attempt too many assumptions would be necessary.

5. Conclusion

The comparison of experiments over a wide range of hydrogen pressure respectively reaction rate shows an increasing CDE yield with decreasing p_{H_2}. At very low p_{H_2} CDE yields >0.9 are reached. The interpretation of the present study is that at high p_{H_2} the Pd surface is not completely covered with CDT and CDD isomers so that CDE can get access to the surface and can be hydrogenated towards CDA thus lowering the CDE yield. At low p_{H_2} respectively low hydrogenation rate we have a regime of dense coverage of the surface by CDT/CDD so that readsorption and subsequent hydrogenation of formed CDE is to a large extent prevented. The preference of CDT/CDD adsorption over CDE is explained by adsorption of CDT/CDD via two double bonds. With this interpretation of the dependence of CDE yield on the hydrogen pressure a consistent hypothesis is presented.

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