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Kinetics and mechanism of butene isomerization/hydrogenation and of 1,3-butadiene hydrogenation on palladium

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ABSTRACT

Combined studies of adsorption and hydrogenation have been carried out using Pd black electrochemically deposited in a loose packed thin layer in order to avoid co-adsorption on a support. Pd black covered with a monomolecular layer of strongly adsorbed hydrogen and exposed to butadiene shows a very low hydrogenation rate, more than two orders of magnitude lower than the rate of hydrogenation of a mixture of butadiene and hydrogen. This result reveals that the second step of hydrogenation according to the reaction scheme of Horiuti and Polanyi via a semi-hydrogenated intermediate needs subsurface hydrogen loading. While the first step towards a surface alkyl requires a negatively charged surface hydride for nucleophilic attack the subsequent electrophilic attack proceeds with a positively charged hydrogen from the subsurface region. Strong support for this view is given by the kinetics of isomerization/hydrogenation of *cis*-2-butene which shows at low hydrogen pressure fast isomerization and slow hydrogenation rate. The access of hydrogen to the catalyst surface is regarded as rate determining step of butene respectively butadiene hydrogenation. The consequence of increased hydrogen access to the Pd surface is an enhanced diffusion of hydrogen from surface to subsurface positions thus leading to an increased hydrogenation rate.

Furthermore in the state of selective hydrogenation of 1,3-butadiene towards butenes the surface is densely covered by butadiene.

1. Introduction

For hydrogenation and isomerization of unsaturated hydrocarbons Horiuti and Polanyi [1] proposed a reaction scheme assuming that the hydrogenation of alkenes occurs in two steps. The half-hydrogenated intermediate is regarded as an adsorbed alkyl radical.

At atmospheric pressure and 300 K SFG spectra acquired during C_2H_4 hydrogenation did not give evidence of any resonances which could be attributed to the half-hydrogenated intermediate. Furthermore, π-bonded ethene which is regarded as the most likely reactive species produces only a very small SFG signal in the C—H stretching frequency range, as a consequence of its nearly parallel geometry on the Pd(1 1 1) surface [2,3].

As spectroscopic studies which till now have been applied do not promise any further penetration into the mechanism of hydrogenation of unsaturated hydrocarbons the aim of our study was to use various kinetic experiments in particular those combined with simultaneous adsorption measurements for mechanistic investigations.

The selective hydrogenations of dienes, e.g. 1,3-butadiene, 1,5-cyclo-octadiene and 1,5,9-cyclo-dodecatriene towards the monoenes are of industrial interest. In these cases the competitive adsorption of diene and monoene plays a crucial role for selectivity towards the monoene. In a former study of adsorption [4–7] using Pd black deposited as a thin layer on Pd foil it could be shown that saturation of 1,3-butadiene is reached at an adsorption stoichiometry of about one butadiene molecule to four Pd surface atoms, but for 1-butene already at about one butene molecule to five Pd surface atoms. If the surface at maximum butadiene coverage is exposed to 1-butene no additional adsorption of butene is observed. In the opposite experiment with complete coverage by 1-butene a rather slow but finally complete displacement of butenes by butadiene occurs. The TOF of this displacement is smaller than $10^{-2}\ s^{-1}$ while the selective butadiene hydrogenation including butene desorption at low p_{H_2} shows a TOF of about $1\ s^{-1}$ [7]. These results reveal that a simple displacement in the case of butadiene hydrogenation must be excluded and thus also the concept of the “thermodynamic factor”. Formed butene is immediately desorbed due to the rather high enthalpy of reaction which in the moment of completed hydrogenation is concentrated on the butene molecule just formed. The

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resultant vacant site is not large enough for butene readsorption. Unfortunately at present there is no chance to calculate such complicated adsorption/desorption processes or even to visualize them [8].

Our study using various kinetic experiments in particular those combined with simultaneous adsorption measurements concerns the isomerization and hydrogenation of butenes and the hydrogenation of 1,3-butadiene.

2. Experimental

Selective hydrogenations of dienes respectively of alkynes to alkenes are usually carried out on Pd supported on silica or alumina in gas phase or liquid phase procedure. In all these cases combined studies of adsorption and hydrogenation cannot be carried out because in most cases adsorption on the support is predominant. Therefore we used Pd black electrochemically deposited on a Pd foil in a loose packed thin layer in order to avoid mass transfer limitations.

2.1. Preparation of the catalyst

Pd is deposited on a Pd foil as cathode from aqueous solution of $PdSO_4$ and H_2SO_4 at a current density of 10^{-2} A cm^{-2}. The loaded foil is thoroughly washed with distilled water and dried. The thickness of the foil is 35 μm. The Pd deposit corresponds to 0.8 μm Pd on both side of the foil. Adsorption of N_2, H_2, butene and butadiene and also the kinetics of hydrogenation of the latter two have been studied using this catalyst. However, the small Pd crystallites (diameter of about 25 nm) show reasonable stability only at temperatures below 323 K so that desorption of adsorbed gases could only be carried out for N_2. For adsorption measurements of hydrogen, butadiene, and butene a special procedure as described in Section 3 has been applied to circumvent the problem of cleaning the surface.

Scanning electron micrographs of the Pd black catalyst at low magnification reveal that the electrochemical deposition leads to a dendritic morphology as shown in Fig. 1. Micrographs of higher magnification show that the dendritic microstructure consists of crystallites with an average size of about 25 nm. No changes of morphology have been observed after treatment of this catalyst with hydrogen at 333 K. The Pd 3d XP spectrum of the untreated Pd catalyst (after washing, drying and evacuating) indicates Pd metal and the presence of a PdO overlayer. After mild reduction with 3000 Pa H_2 at 333 K for 2 h PdO is no longer present demonstrating complete reduction.

2.2. Sorption studies

Sorption experiments were carried out by the static method at temperatures not higher than 323 K. Fig. 2 shows the experimental unit, which contains a GC/MS unit for the analysis of the gas in the adsorption cell. A low volume chamber allows the removal of very small samples so that the pressure and composition of the content of the adsorption cell is only marginally changed. This small sample is diluted with helium and conducted to the GC/MS unit for quantitative analysis. The construction of the gas sampling system avoids stagnant volumes, so that the whole amount of the gas sample is available for the analysis. For all studies the fraction of butene includes all isomers. The amounts of substance of adsorbed and desorbed gases were evaluated by mass balances.

This experimental unit is suited for the study of multicomponent adsorption but also for the study of chemical reactions in the adsorption cell.

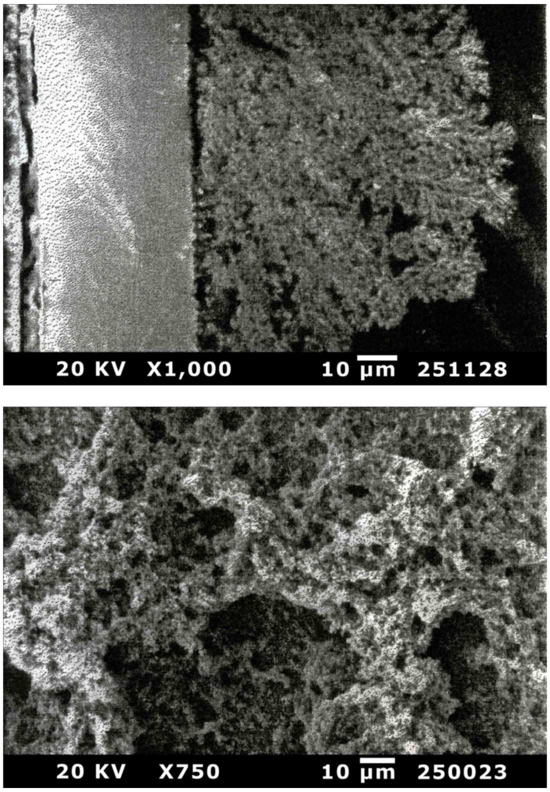


Fig. 1. Scanning electron micrographs of Pd black on Pd foil.

2.3. Kinetic studies

The vapor phase hydrogenation of 1,3-butadiene on Pd black/Pd foil was studied using a continuously operated recycle reactor (CST-reactor), realized by a jet stream through a nozzle at the reactor inlet. With this CST-reactor reaction rates could be directly measured, Fig. 3. A more detailed description of this type of recycle reactor is given in Ref. [9].

In contrast to the butene hydrogenation the rate of isomerization is extremely high so that the highly active Pd black layer of about 10 μm on Pd foil was not suitable to study the kinetics of isomerization. Therefore, we used an egg-shell catalyst with 0.1% Pd on Al_2O_3, cylindrical type: diameter 1.2 mm, length about 5 mm, length of active layer (40–80 μm). Even for this catalyst with highly dilute Pd the isomerization of butenes is strongly influenced by

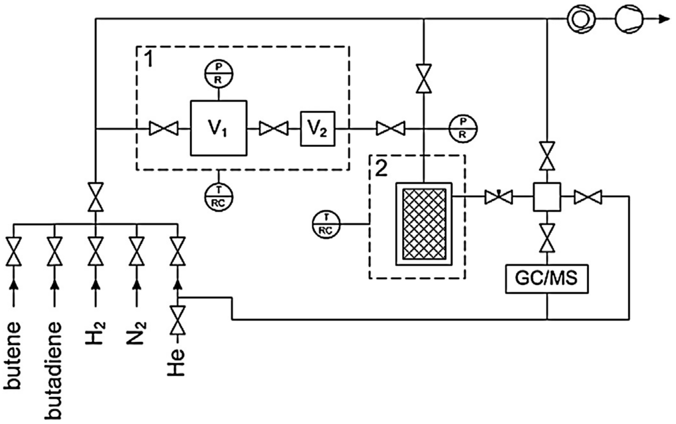


Fig. 2. Experimental unit for combined adsorption and reaction rate studies.

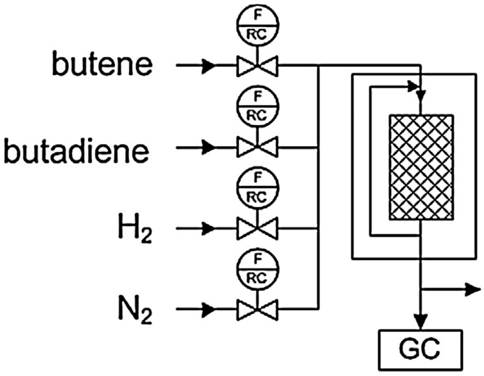


Fig. 3. Experimental unit equipped with a continuously operated recycle reactor.

mass transfer. However this effect could be taken into account for discussion as described in Section 3.8.

3. Results

3.1. *Adsorption of dinitrogen*

The catalyst surface was determined by dinitrogen adsorption applying the BET method. The space requirement of one adsorbed dinitrogen molecule is 1.63 nm^2 so that for polycrystalline Pd the adsorption stoichiometry N_2/Pd_s is approximately 0.5. The specific surface of the porous Pd black layer is $S_{Pd} = 11\ m^2/g$(deposited Pd black) for the freshly prepared catalyst after washing with distilled water, drying and evacuating as well before and after treatment with hydrogen (2 h at $p(H_2) = 3000$ Pa, $T = 333$ K). The surface of the Pd foil is negligible.

For polycrystalline Pd the specific number of Pd-atoms of the surface is $1.27 \times 10^{19}\ m^{-2}$ and the specific number of Pd atoms of the bulk is $5.66 \times 10^{21}\ g^{-1}$. With these data the degree of dispersion of Pd black is $D_{Pd,black} = 0.024$. With the assumption of spherical particles the mean diameter of Pd particles for Pd black on Pd foil comes out at $d = 37$ nm. From scanning electron micrographs the roughly estimated diameter ($d \approx 25$ nm) is in reasonable agreement.

3.2. *Adsorption of dihydrogen*

Adsorbed N_2 from BET measurement is removed by evacuation with a turbo diffusion pump down to 10^{-8} hPa for 24 h. Then the catalyst is loaded in small steps with H_2 until a constant pressure is reached resulting in an S-shaped adsorption curve 1 as shown in Fig. 4. The hydrogen uptake arises from the strongly bound H on the surface of ~0.8 eV per Pd atom and the dissolved H in the subsurface of ~0.4 eV per Pd atom [10]. The S-shape of this curve is interpreted by the reduction of adsorbed oxygen according to

$$PdO + H_2 \rightarrow Pd + H_2O$$

This reduction leads to a shift of the adsorption curve 1 towards a higher pressure provided that water is completely desorbed. This shift of approximately 0.6 hPa gives the amount of desorbed water and corresponds to about 0.14 O/Pd. Curve 2 shows the uptake of hydrogen after evacuation at 303 K down to 10^{-7} hPa so that water and dissolved hydrogen are removed thus giving the dissolved H in the bulk. Curve 3 shows the third uptake of dihydrogen after repeated vacuum treatment thus reproducing curve 2. The difference between curve 1 and 2 is attributed to irreversibly adsorbed hydrogen. For calculating the amount of adsorbed dihydrogen curve 1 must be corrected by subtracting the shift (0.6 hPa) caused by PdO reduction. This correction is done for elevated pressure with the assumption of complete PdO reduction (curve 1^*). In this range the difference of H_2 uptake, curve 1^*/curve 2, is 0.13 Nml/g normalized to $T = 298$ K; $p = 1$ bar. Comparison with the monolayer of N_2 estimated by BET at 0.113 Nml/g indicates an approximate monolayer of strongly bound hydrogen. Since dihydrogen is dissociatively adsorbed on Pd every Pd atom of the surface obviously carries one H atom. Adsorption experiments with butene respectively butadiene provide a further and independent method of estimating the amount of adsorbed dihydrogen (see following sections).

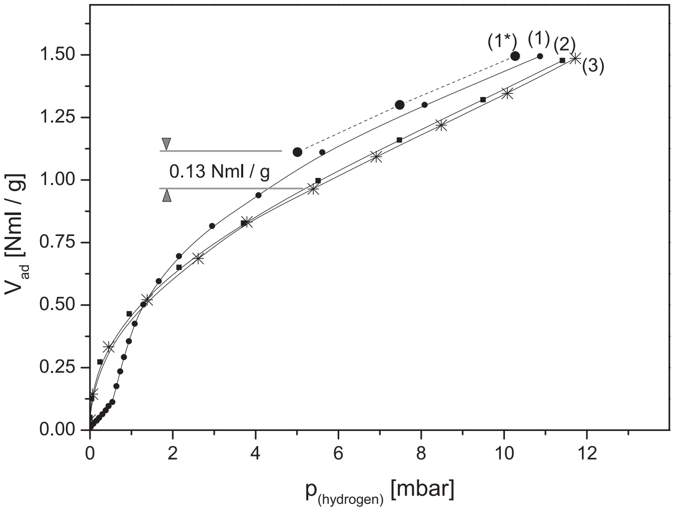


Fig. 4. Adsorption and dissolution of hydrogen on/in the Pd black/Pd foil catalyst, $T = 303$ K.

3.3. *Adsorption of butene*

Before loading of butene the Pd black/Pd foil was reduced with dihydrogen at 333 K, 3000 Pa for 2 h, followed by high vacuum treatment for 24 h. Fig. 5 shows the amount of adsorbed butene versus the total pressure in the adsorption chamber. The data points were registered when the change of pressure in the adsorption chamber was negligible. At the beginning of butene addition fast adsorption up to 0.02 Nml/g is observed. Up to a pressure of 3 hPa the analysis of the gas phase shows 100% butane indicating butene hydrogenation by strongly adsorbed hydrogen. The slight S-shape

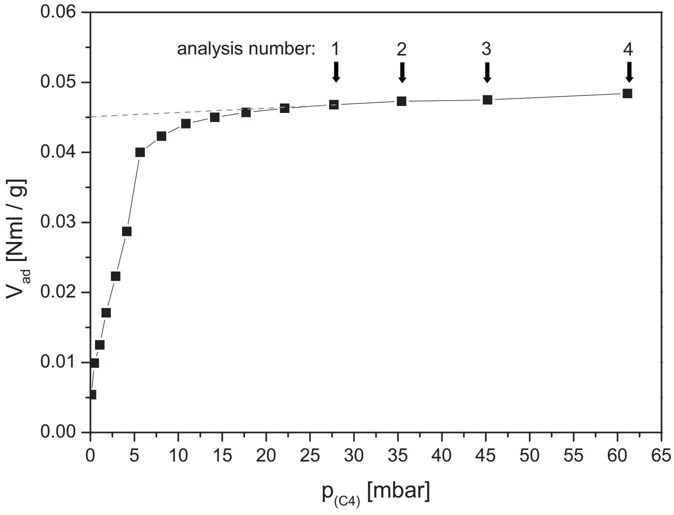


Fig. 5. Adsorption and hydrogenation of butene on the hydrogen precovered Pd black/Pd foil catalyst, $T = 303$ K.

Table 1
Preloading of hydrogen calculated from Fig. 5.

No of analysis	Fraction of butane in gas phase (%)	Calculated preloading of hydrogen (Nml/g)
1	17	0.11
2	13.9	0.11
3	14.9	0.16
4	8.3	0.11

of the adsorption curve is due to simultaneous hydrogenation and adsorption of butene. With further butene addition the amount of adsorbed butene increases up to 0.045 Nml/g. In this period the content of butane in the gas phase decreases from 17 to 8.3% as listed in Table 1 corresponding to a consumption of adsorbed hydrogen of 0.12 Nml/g in agreement with the amount of adsorbed dihydrogen estimated from the data of dihydrogen sorption presented in Fig. 4. The conclusion is that adsorbed hydrogen is completely removed by reaction with butene. Subtraction of the corresponding pressure difference gives the corrected adsorption curve versus the butene pressure which is presented in Fig. 6.The adsorbed butene referred to the number of surface atoms of Pd is for saturation $N_{\text{Butene}}/N_{\text{Pd,s}} = 0.2$ corresponding to a space requirement of 5 Pd atoms of the surface for one butene molecule.

High vacuum treatment at $T = 303$ K causes only a relative small desorption of butene so that subsequent adsorption of butene results only about 10% of the first adsorption. Butene can only be totally removed by hydrogenation. Then after vacuum treatment the butene coverage could be reproduced.

3.4. *Adsorption of butadiene*

The adsorption studies of 1,3-butadiene were carried out in the same way as for butene, Fig. 7. In a first period of butadiene addition up to an adsorption of 0.08 Nml/g also a fast adsorption of butadiene is observed. Then hydrogenation to butene occurs which is adsorbed and subsequently hydrogenated to butane so that in this first period only butane is detected in the gas phase. With increasing addition of 1,3-butadiene butene and butane are formed and 1,3-butadiene is adsorbed. Finally the adsorption of 1,3-butadiene approaches saturation at 0.056 Nml/g. This maximum amount of adsorbed 1,3-butadiene referred to the number of surface atoms of Pd is $N_{\text{butadiene}}/N_{\text{Pd,s}} = 0.25$ corresponding to a space requirement of 4 Pd atoms of the surface for one 1,3-butadiene molecule which is 20% lower than for butene.

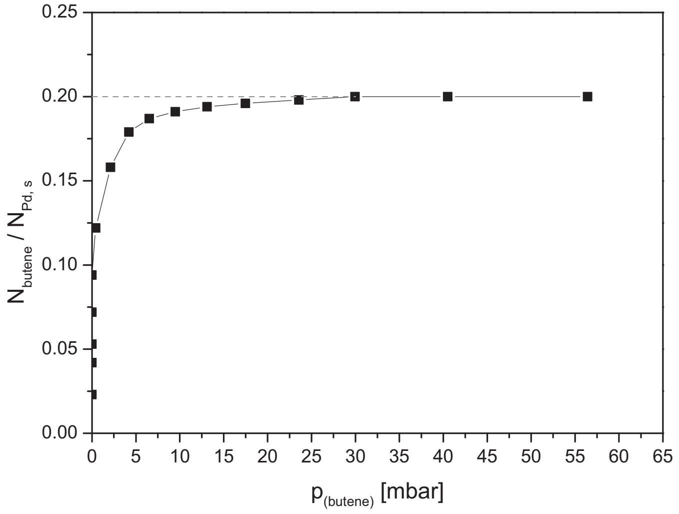


Fig. 6. Adsorption of butene on the Pd black/Pd foil catalyst, $T = 303$ K.

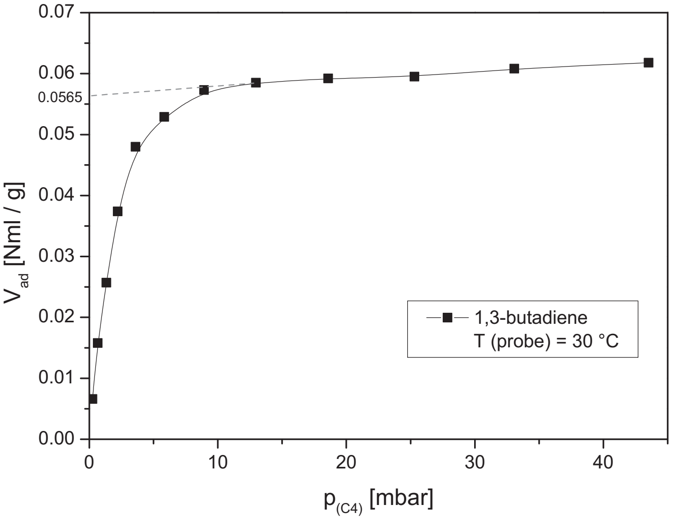


Fig. 7. Adsorption and hydrogenation of 1,3-butadiene on the hydrogen precovered Pd black/Pd foil catalyst, $T = 303$ K.

In another experiment after hydrogen treatment and evacuation down to 10^{-7} hPa at start a sevenfold excess of 1,3-butadiene was added. Fig. 8 shows the course of 1,3-butadiene adsorption and butene formation. As no butane could be detected in the gas phase butenes are formed with 100% selectivity. Adsorbed 1,3-butadiene prevents the readsorption of butene and its hydrogenation to butane. The rate of butene formation is very low, for complete coverage with strongly adsorbed hydrogen at the start of the experiment (tangent in Fig. 8) 1.06×10^{-5} mol/g h. This rate is to be compared with the hydrogenation rate in a continuously operated butadiene hydrogenation as presented in Section 3.6.

3.5. *Displacement of butene by butadiene*

In order to study the role of displacement of butene by butadiene for the selectivity of butadiene hydrogenation in view of the "thermodynamic factor" experiments were carried out recently which results are mentioned in Section 1. Since some aspects of these experiments are of interest for the discussion of the present study Fig. 9 shows the course of gas phase composition during this displacement. The loading with butene took place in the same way as described in Section 3.3. Adsorbed butene, monolayer 0.045 Nml/g, is completely desorbed forming the more

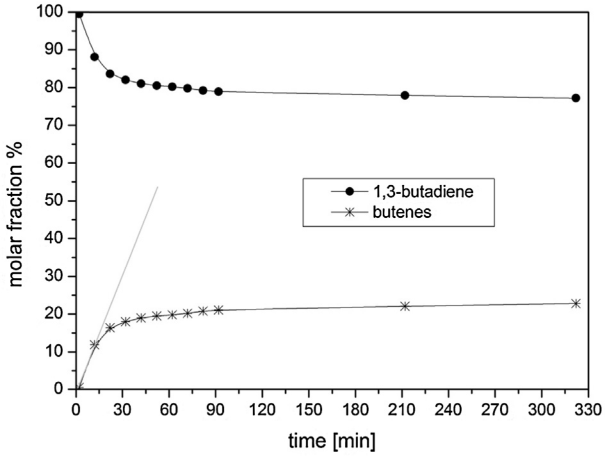


Fig. 8. Hydrogenation of 1,3-butadiene by hydrogen precovered Pd black/Pd foil, fractions of 1,3-butadiene and of butene vs. time $T = 303$ K.

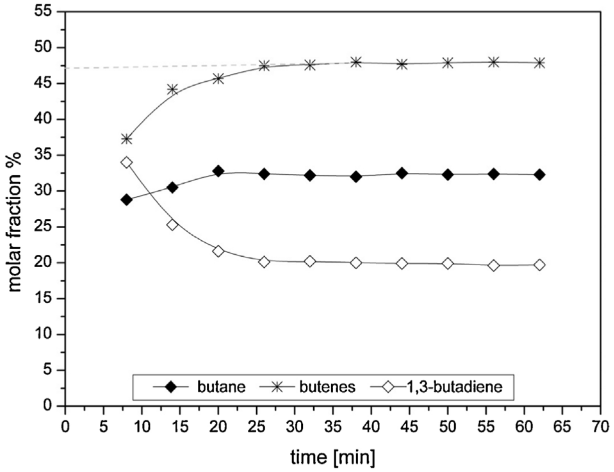


Fig. 9. Displacement of adsorbed butene by 1,3-butadiene $T = 303$ K.

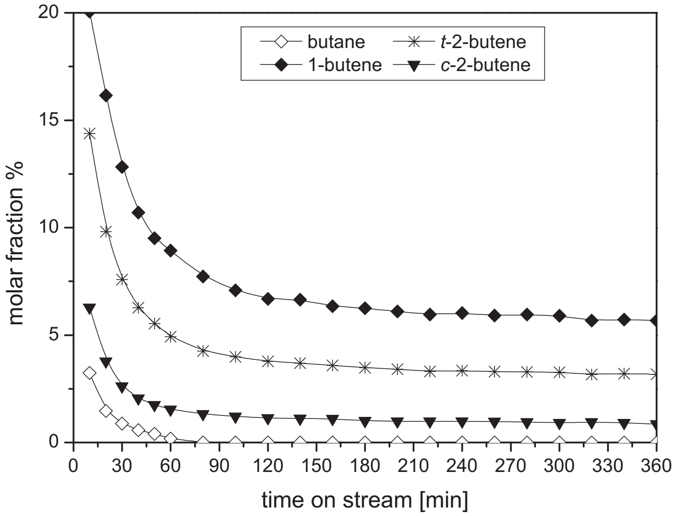


Fig. 10. Hydrogenation of 1,3-butadiene, fractions vs. time on stream $p^0_{H_2} = 1000$ Pa, $p_{C_4H_6} = 1000$ Pa, $T = 318$ K, $p_{tot} = 2.5$ bar, carrier gas N_2.

dense butadiene monolayer of 0.057 Nml/g. The fraction of butane results from the dehydrogenation of the catalyst by butene. Its slight increase corresponds with the higher adsorption density of butadiene compared to that of butene. The complete desorption of butene reveals that its adsorption under these conditions is not accompanied by dehydrogenation to carbonaceous species on the surface even in the absence of hydrogen.

Pd catalysts may contain carbonaceous deposits resulting from early decomposition of hydrocarbons [11]. However it should be mentioned that on supported model catalysts Pd/Fe_3O_4/Pt(1 1 1) 2-butene could be decomposed by heating to 485 K resulting in a sub-monolayer of strongly dehydrogenated carbonaceous species [12]. This makes understandable that at the much lower temperature (303 K) of our experiment no dehydrogenation of butene was observed. However, this result cannot exclude the gradual formation of carbonaceous species during long term butadiene or butene hydrogenation.

3.6. Continuous hydrogenation of 1,3-butadiene

Using the continuously working recycle reactor the Pd black/Pd catalyst was tested under a pressure of 1000 Pa hydrogen and 1000 Pa 1,3-butadiene for 14 h. A nearly constant activity and selectivity is reached after 2 h as shown in Fig. 10. With the catalyst treated in this way for 2 h the reaction rate of butadiene hydrogenation was studied depending on the pressure of hydrogen. Fig. 11 shows a linear increasing rate of butadiene hydrogenation to butene while the rate of butane formation is negligible up to $p_{H_2} \approx 800$ Pa. Further increase of hydrogen pressure results in a considerable increase of the rate of butadiene hydrogenation and a dramatic increase of hydrogenation to butane. This may be interpreted by a sudden break-up of the dense layer of butadiene causing a free access of dihydrogen to the surface and also a chance of butene readsorption.

3.7. Stability of the catalyst

The surface of the Pd black/Pd foil catalyst is not changed by loading the catalyst with hydrogen followed by vacuum treatment, as shown in Fig. 4. However, the surface determined by BET analysis decreases after removal of butene or butadiene by hydrogenation. This may be due to the considerable reaction heat of butene or butadiene hydrogenation which causes reconstruction of the Pd black layer. However, at reduced surface the obtained data of hydrogen, butene and butadiene coverage referred to the number of surface atoms of Pd, estimated by BET, are in agreement with the results reported above. For a catalyst which was used for three experiments of butene adsorption, every time regenerated by hydrogenation of the butene layer, the surface was reduced to one third of the starting value. This is in agreement with the test run of butadiene hydrogenation as reported in Section 3.6.

3.8. Kinetics of c-2-butene isomerization/hydrogenation on Pd/Al_2O_3 catalyst

The Horiuti–Polanyi mechanism characterized by a series of successive hydrogenation-dehydrogenation steps is generally accepted for alkene conversion.

Scheme 1 shows this mechanism for the geometrical isomerization and hydrogenation of butenes. In the first step a half-hydrogenated surface species is formed which is the intermediate for both *c*-*t*-isomerization and hydrogenation to butane. Therefore, kinetic studies of isomerization may contribute to the understanding of the hydrogenation of butene to butane.

As shown in Fig. 12a even at very low hydrogen pressure an exceptionally fast reaction rate of isomerization of *c*-2-butene is observed. With increasing p_{H_2} the increase of rate gradually slows

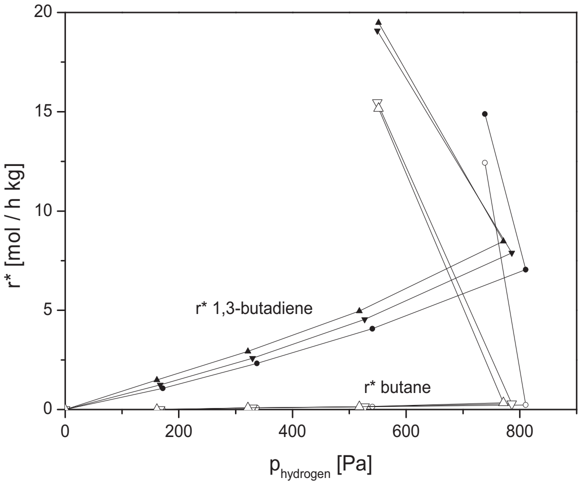
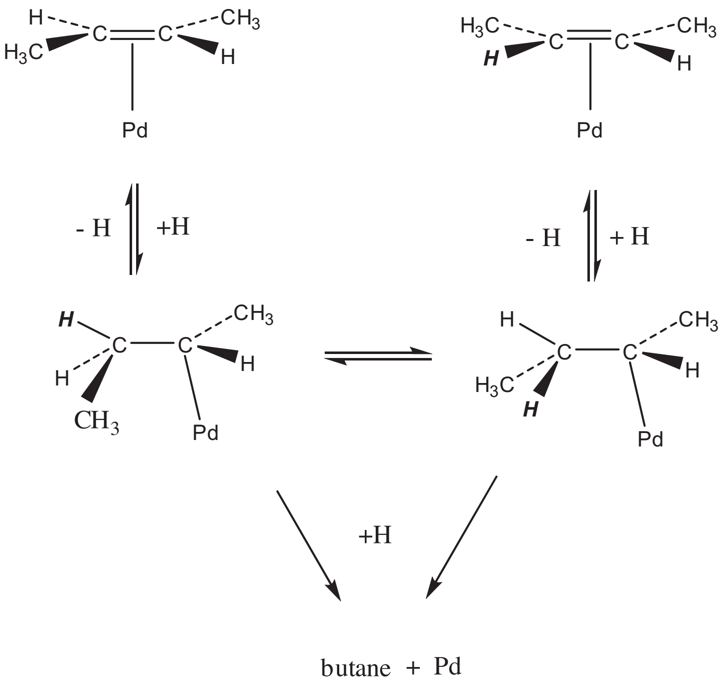


Fig. 11. Hydrogenation of 1,3-butadiene on Pd black/Pd foil, reaction rate of C_4H_6 consumption and C_4H_{10} formation vs. time, $P_{C_4H_6} = 400$ Pa, $p_{C_4H_8} = 2000$ Pa, $T = 318$ K, $p_{tot} = 2.5$ bar, carrier gas N_2.



Scheme 1. Horiuti–Polanyi mechanism for butenes.

down and finally the rate arrives at independency. The much lower rate of butene hydrogenation increases by a hydrogen order of somewhat higher than one as presented in Fig. 12b. Due to the very fast isomerization rate we expect strong influence of mass transfer processes as explained elsewhere [7]. This influence of mass transfer is demonstrated schematically by Fig. 13 and the plot of isomerization rate as function of *c*-2-butene pressure at constant p_{H_2}, Fig. 14. At very low p_{H_2} the slope of the rate of isomerization decreases with increasing *c*-2-butene pressure which may finally approach a constant value. Therefore we assume that at high $p_{\text{c-2-butene}}$ the reaction occurs over the entire range of the Pd covered active layer of the catalyst. Furthermore it may be assumed that the intrinsic rate is independent of $p_{\text{c-2-butene}}$. However at elevated p_{H_2} the reaction rate approaches a linear increase of $r_{\text{isom.}}$ as function of $p_{\text{c-2-butene}}$. In this case it is assumed that the reaction occurs at a small part of the active layer as demonstrated in Fig. 13. Then the rate $r_{\text{isom.}}$ is determined by mass transfer through the hydrodynamic boundary layer around the catalyst pellet. For this case a linear relationship of mass transfer and $p_{\text{c-2-butene}}$ is expected. Due to the small part of active layer effective for the reaction the intrinsic rate of isomerization is expected as much higher than shown by Fig. 12a. Furthermore we must realize that the isomerization rate includes the addition of hydrogen, the rotation of the semi-hydrogenated intermediate and the β-hydride elimination. As we can assume that the intermediate can undergo hydrogen abstraction before rotation the rate of hydrogen addition must be assumed as higher than the rate of isomerization.

The situation is different for the hydrogenation of butenes towards butane which includes the second step of H-addition. As shown in Fig. 12b this rate is rather low. As the consumption of hydrogen is low and the effective diffusion coefficient is about an order of magnitude higher for H_2 than for butene we expect nearly constant p_{H_2} over the entire range of the active layer as demonstrated in Fig. 13. In this case the intrinsic reaction rate is approximately observed with its hydrogen order of somewhat higher than one. Since the rate of isomerization indicates a very fast hydrogenation towards the semi-hydrogenated intermediate this step is by no means a rate determining step in butene hydrogenation as assumed by Zaera [13,14]. The steady state concentration respectively the lifetime of the semi-hydrogenated intermediate which depends on the ratio of the rate constants of H-addition and H-abstraction may be very low so that a spectroscopical detection seems hardly possible.

4. Discussion

4.1. Kinetics and reaction mechanism of alkene hydrogenation

As already discussed in Ref. [15] the action of hydrogen depends on the specific bonding of H in different positions on the surface and in the surface-near region. π-Coordinated alkene is prone to nucleophilic attack by surface hydride which generates a semihydrogenated intermediate. Subsequent electrophilic attack at the α-C atom requires a positively charged H from the surface-near region which could occupy an octahydral hole next to this intermediate.

Recently [16,17] experimental and theoretical evidence for the role of subsurface hydrogen in the second hydrogenation step were reported. A very informative survey is given of these studies using Pd nanocrystallites (6 nm) supported on ordered Fe_3O_4 film on Pd(1 1 1) and analysis of both strongly adsorbed surface hydrogen and subsurface hydrogen by NRA [18]. The main result was that the catalyst preloaded with deuterium shows for further addition of D_2/cis-butene sustained cis/trans isomerization but decreasing activity of hydrogenation to butane. The conclusion was that the second step of hydrogenation needs subsurface hydrogen. Internal diffusion of D respectively H from the surface to the subsurface region must be regarded as a crucial step.

As explained in Section 3.4 and demonstrated by Fig. 8 the rate of butadiene hydrogenation with strongly adsorbed hydrogen in an approximate monolayer and completely removed hydrogen of the bulk is rather low, $1.06 \cdot 10^{-5}$ mol/g h, whereas the rate of continuously operated butadiene hydrogenation at $p_{H_2} = 100$ Pa is about 10^{-3} mol/g h, which is two orders of magnitude higher than by reaction with surface hydrogen. This is another strong support for the assumption that hydrogen from the subsurface region is necessary

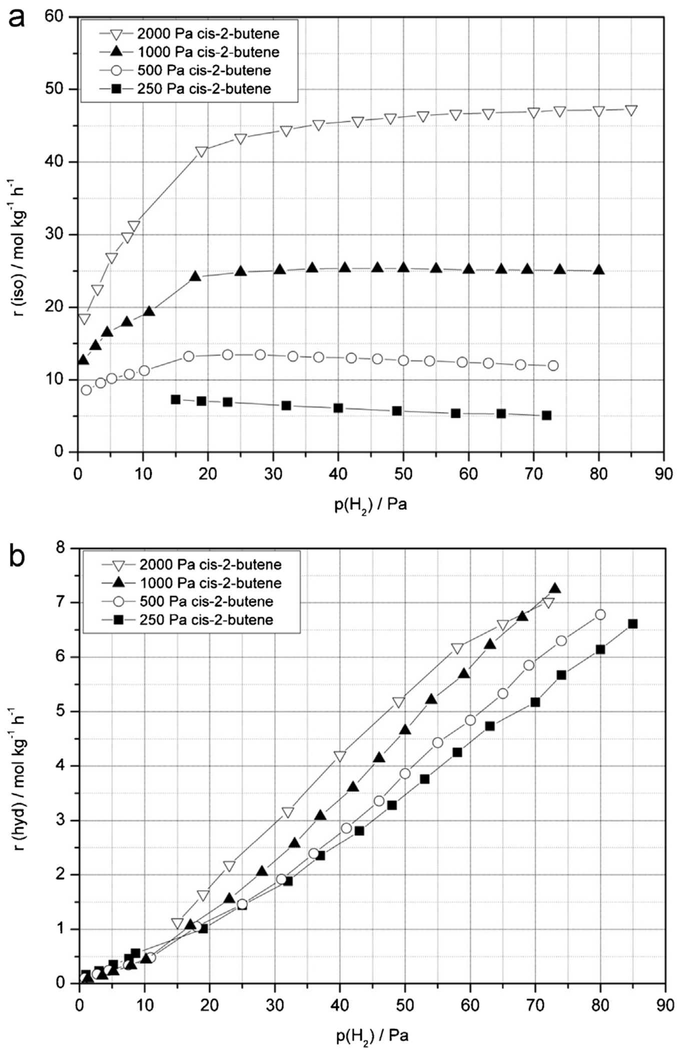


Fig. 12. (a) Reaction rate of isomerization of c-2-butene for varied pressures of c-2-butene, $T = 333$ K, $p_{tot} = 3.5$ bar, carrier gas He. (b) Reaction rate of c-2-butene hydrogenation towards butane for varied pressures of c-2-butene, $T = 333$ K, $p_{tot} = 3.5$ bar, carrier gas He.

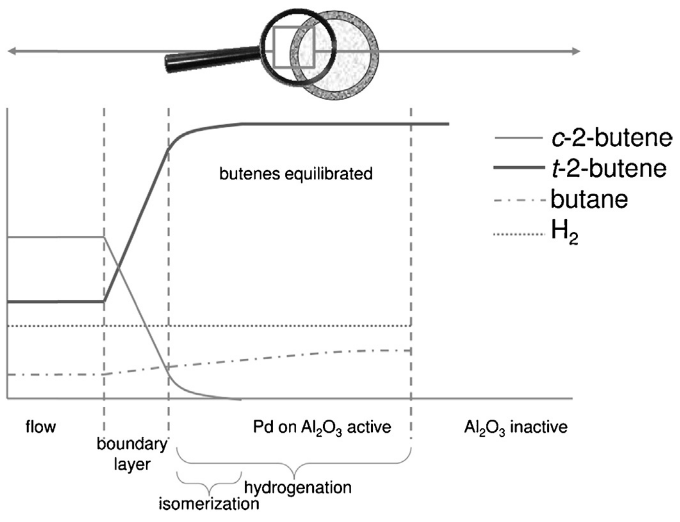


Fig. 13. Concentration profiles along a section through a catalyst pellet for explanation of mass transfer influence on reaction rate.

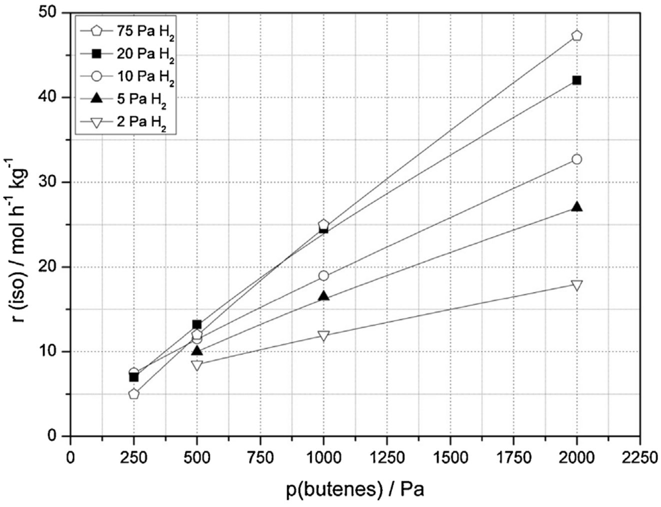


Fig. 14. Isomerization rate as function of c-2-butene pressure for constant p_{H_2}. Reaction conditions see Fig. 12a.

for the hydrogenation of adsorbed semi-hydrogenated species. The hydrogenation rate in the case with strongly adsorbed hydrogen at the surface is extremely low because of the crucial transfer of hydrogen from the surface with high energy of adsorption to the subsurface characterized by low energy of adsorption.

On the basis of our kinetic experiments of isomerization and hydrogenation of cis-2-butene further conclusions can be drawn. Comparison of Fig. 12a (isomerization) and Fig. 12b (hydrogenation) shows that isomerization is much faster than hydrogenation, in particular at low p_{H_2} by several orders of magnitude. As shown in Fig. 12b at very low p_{H_2} the hydrogenation of alkenes is higher than first order with respect to hydrogen approaching first order at elevated p_{H_2} as observed in several other studies [7]. This leads to the assumption that at very low p_{H_2} loading of sub-surface hydrogen is a crucial step as discussed above. Due to the variety of different sites of the subsurface region a distribution of energy of hydrogen corresponding to different activity of reaction is expected. This suggests an increased hydrogenation rate of the second step with increasing loading of subsurface sites with hydrogen.

Furthermore these results and discussions give rise to interpret the rate determining step of alkene respectively alkadiene hydrogenation. We assume the access of dihydrogen to the catalyst surface which is nearly densely covered by hydrocarbons as rate determining step. The rate of hydrogen access can be regarded as proportional to the probability of collisions of hydrogen molecules with the surface. Early studies of Bates et al. [19] have given strong support for this assumption as in the reaction of 1,3-butadiene with mixtures of hydrogen and deuterium the hydrogen/deuterium exchange $H_2 + D_2 \Leftrightarrow 2HD$ is inhibited in the presence of butadiene and hence dissociatively adsorbed hydrogen is immediately consumed for hydrogenation. Valcarcel et al. [20] studied simultaneously the hydrogenation of 1,3-butadiene on Pd(1 1 0) of a single crystal and the dissolution of hydrogen in the bulk phase of this crystal. In the period of selective hydrogenation towards butenes the dissolution of hydrogen in the bulk is nearly zero in accordance with the result of Bates et al.

The discussion above has led to the conclusion that the second hydrogenation step according to the mechanism of Horiuti and Polanyi needs high hydrogen loading of subsurface sites. Then it can be expected that the sites of the surface are densely covered with hydrogen and alkenes so that H_2 access for dissociative chemisorption must be assumed to be restricted.

The consequence of increased hydrogen access to the Pd surface is an enhanced diffusion of H from surface to subsurface positions leading to an order >1 with respect to hydrogen and at elevated p_{H_2} to a first order.

4.2. Selectivity of butadiene hydrogenation

It is well known that 100% selectivity towards butenes is obtained when butadiene is present in the gas phase even if its concentration is very small. This has been interpreted by a much stronger adsorption of butadiene with respect to butenes at first glance suggesting an immediate displacement of formed butenes by butadiene. However, it could be shown that the displacement of adsorbed butene on the Pd_{black}/Pd catalyst by butadiene is by two orders of magnitude slower than in the observed hydrogenation of butadiene. This has been interpreted by fast desorption of butenes due to the rather high enthalpy of reaction which in the moment of reaction is concentrated on the butene molecule just formed. As adsorbed butene has a higher space requirement than butadiene and a much lower energy of adsorption the chance of butene readsorption is nearly zero.

The partial hydrogenation of 1,3-butadiene leads by 1,2-hydrogenation to 1-butene and by 1,4-hydrogenation to the geometrical isomers *c*-2-butene and *t*-2-butene. The ways to these isomers depend in a complicated manner on the structure of the adsorption layer and the availability of hydrogen. The complexity of butadiene on Pd surfaces allows for a large number of adsorbate configurations possibly including π-allyl species [7,19,21–23] so that future spectroscopic investigations are needed for a detailed discussion of the reaction mechanism.

5. Conclusion

Pd black covered with a monomolecular layer of strongly adsorbed hydrogen and exposed to butadiene shows a very low hydrogenation rate, more than two orders of magnitude lower than the rate of hydrogenation of a mixture of butadiene and hydrogen. This result reveals that the second step of hydrogenation according to the reaction scheme of Horiuti and Polanyi needs hydrogen loading near the surface. While the first step towards a surface alkyl requires a negatively charged surface hydride for nucleophilic attack the subsequent electrophilic attack proceeds with a positively charged hydrogen from the subsurface region.

The access of hydrogen to the catalyst surface is regarded as rate determining step of butene respectively butadiene hydrogenation. The consequence of increased hydrogen access to the Pd surface is an enhanced internal diffusion of H from surface to subsurface positions thus leading to an increased hydrogenation rate.

The high selectivity of 1,3-butadiene hydrogenation to butenes is explained by immediate desorption of formed butenes and the hindrance of butene readsorption by dense coverage of butadiene.

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