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Atmospheric pressure studies of selective 1,3-butadiene hydrogenation on Pd single crystals: effect of CO addition

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Abstract

The selective hydrogenation of 1,3-butadiene on Pd(111) and Pd(110) model catalysts was studied at atmospheric pressure in the temperature range 298–373 K. In the initial stages of the reaction, 1-butene, *trans*-2-butene, and *cis*-2-butene were the main reaction products. After full 1,3-butadiene consumption, 1-butene was readsorbed and reacted to *n*-butane via hydrogenation and to *trans*/*cis*-2-butene via isomerization. Because hydrogenation was favored on Pd(111), Pd(110) exhibited a higher selectivity for butene formation. Increasing the reaction temperature accelerated both processes, and hydrogenation was favored at long reaction times. Addition of small amounts of CO drastically changed the selectivity on Pd(110); that is, the hydrogenation to *n*-butane was completely suppressed, whereas the hydrogenation to butenes and 1-butene isomerization to *cis*- and *trans*-2-butene were hardly affected. This can be rationalized by considering that CO reduces the hydrogen surface concentration to a level that is still sufficient for 1,3-butadiene hydrogenation and 1-butene isomerisation but too low for butene hydrogenation. In contrast, on Pd(111), catalytic activity basically vanished in the presence of CO traces. Possible reaction mechanisms are discussed.

Keywords: Selective hydrogenation; Palladium; Low index single crystal surfaces; Butadiene; Carbon monoxide; Model catalysts

1. Introduction

Selective hydrogenation is an important process both in homogeneous and heterogeneous catalysis. Its primary target is the hydrogenation of a specific unsaturated bond (e.g., C=C, C≡C or C=O), while leaving other unsaturated bonds within the molecule (or in other molecules) unaffected. For instance, in the course of the production of polybutene from 1-butene, traces of 1,3-butadiene must be selectively converted to 1-butene, whereas isomerization of 1-butene to 2-butenes or further hydrogenation to *n*-butane should be prevented to avoid quality loss of the polymer [1]. (The unwanted dienes are by-products of the production of unsaturated hydrocarbons by thermal cracking of petroleum [2–4].) Similarly, in alkylation processes used to produce high-octane gasoline from butanes and butenes, 1,3-butadiene "contamination" would increase the amount of undesired heavy alkylation gas oil[1] [2] and thus must be transformed to butene [5]. In contrast to the polymerization mentioned earlier, 2-butene produces gasoline of higher octane number than 1-butene, and there is no need to suppress the isomerization of 1-butene to 2-butene.

Because of the technological importance of 1,3-butadiene hydrogenation, this reaction has attracted much attention, and palladium-based catalysts are frequently used [6,7]. Previous studies have shown that the Pd particle size, support acidity, and presence of transition metals have a significant influence on the activity and selectivity of the hydrogenation reaction and also affect butene isomerization [8,9]. For

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[1] Presence of diene leads to gum formation which causes technical problems.

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Pd/Al_2O_3 and Pd/SiO_2, Boitiaux et al. [10] reported increasing activity with increasing particle size (1–4 nm), in agreement with results on Pd/activated carbon reported by Tardy et al. [8]. In contrast, Sarkany et al. [11] did not observe a correlation between catalytic activity and particle size on Pd/ZnO catalysts, in agreement with Boitiaux et al. [12] for Pt catalysts for liquid phase hydrogenation. These discrepant results may originate in part from the high surface area and porous structure of the catalysts applied, which prevent detailed characterization of the exact surface structure and composition.

This can be circumvented in part by using planar model catalysts that are well accessible to surface-sensitive techniques. However, only a few model studies of 1,3-butadiene hydrogenation were carried out to date. Massardier et al. studied the hydrogenation of 1,3-butadiene over Pd and Pt single crystals [13,14] showing that palladium is more active and much more selective in 1-butene than platinum. This may be due to the different adsorption modes of 1,3-butadiene, as determined under ultra-high vacuum (UHV) by high-resolution electron energy loss spectroscopy (HREELS). It was observed that 1,3-butadiene is di-π bonded on Pd(111) but di-σ bonded on Pt(111) at 300 K [15,16].

In an effort to gain more information on kinetic parameters of 1,3-butadiene hydrogenation and to get some insight into the reaction mechanism, we have studied the reaction on Pd(111) and Pd(110) single crystals using a UHV-compatible atmospheric-pressure reaction cell. In particular, the effect of the reaction temperature and of CO coadsorption were examined. Adding a small amount of CO strongly changed the activity and selectivity; for example, on Pd(110), hydrogenation to n-butane was suppressed whereas the hydrogenation to butenes and their isomerization reactions were hardly affected.

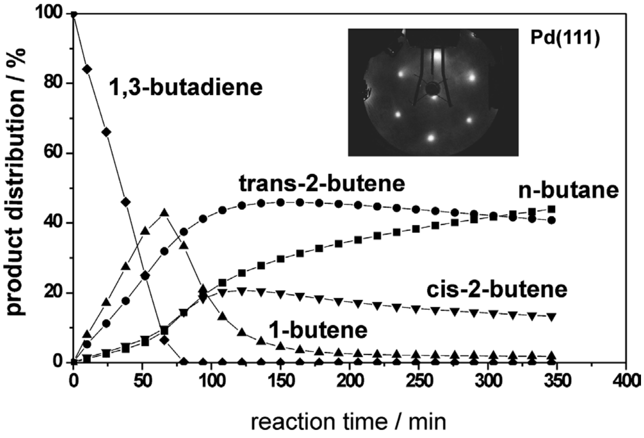

Fig. 1. Product distribution versus reaction time for 1,3-butadiene hydrogenation on Pd(111) at 298 K. The inset shows the LEED pattern of the clean surface.

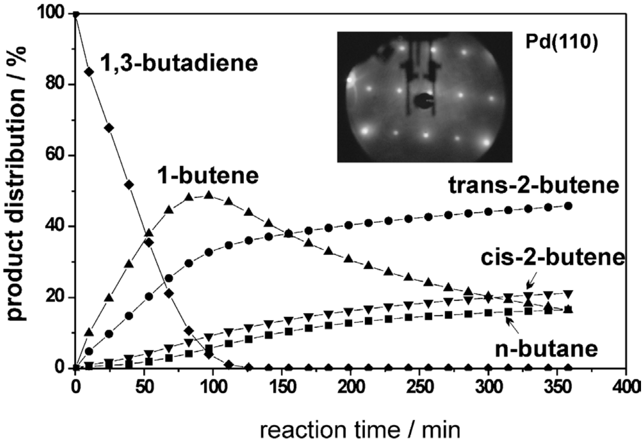

Fig. 2. Product distribution versus reaction time for 1,3-butadiene hydrogenation on Pd(110) at 298 K. The inset shows the LEED pattern of the clean surface.

2. Experimental

The experiments were carried out in a UHV surface analysis system combined with a UHV high-pressure reaction cell, very similar to the setup described elsewhere [17,18]. For sample characterization, the UHV section (base pressure $\approx 1 \times 10^{-10}$ mbar) was equipped with low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), and temperature-programmed desorption (TPD). The crystals were mounted between Ta wires and could be resistively heated to 1300 K and cooled with liquid nitrogen to 90 K. Pd(111) and Pd(110) surfaces were cleaned by a sequence of annealing to 1100 K, Ar ion etching (beam voltage 900 V at 6×10^{-6} mbar Ar at 298 K), heating to 1100 K, oxidation during cooling down in 5×10^{-7} mbar O_2 between 1100 and 600 K, and a final flash to 1100 K in UHV. After cooling to 90 K, the well-ordered surface structures were confirmed by LEED (see inset in Figs. 1 and 2).

The clean samples were then transferred under UHV to the reaction cell where catalytic measurements were performed at atmospheric pressure. During transfer, the sample holder is inserted in an arrangement of three differentially pumped spring-loaded Teflon seals, which separates the reaction cell from the UHV chamber. The model catalyst was then contacted with the reaction mixture ($P_{\text{1,3-butadiene}}$, 5 mbar; P_{H_2}, 10 mbar; Ar added up to 1 bar) at temperatures from 298 to 373 K. To avoid β-palladium hydride formation, the hydrogen pressure was kept well below the required threshold pressure. The kinetic measurements were carried out in a batch mode with the gas recirculated over the catalyst by a metal bellows pump (reactor volume 755 cm^3 exchanged 4–5 times per minute). The reaction products were analyzed by on-line gas chromatography (GC), using a HP-PLOT/Al_2O_3 (50 m × 0.53 mm) capillary column and an flame ionization detector (FID). Retention times and sensitivity factors for the reactant and the products were calibrated using a number of different gas mixtures.

3. Results

3.1. Pd(111) and Pd(110) single crystals

The selective hydrogenation of 1,3-butadiene is a *structure-sensitive* reaction that has four possible products (1-butene, *trans*-2-butene, *cis*-2-butene, and *n*-butane). Figs. 1 and 2 show the product distribution for our "standard conditions" ($P_{\text{1,3-butadiene}}$, 5 mbar; P_{H_2}, 10 mbar; P_{Ar}, 1000 mbar) on Pd(111) and Pd(110), respectively, both at 298 K. In the early stages of the reaction (at short reaction times), 1,3-butadiene is the dominant adsorbed species for both catalysts and is hydrogenated to the different butenes (1-butene, *trans*-2-butene, and *cis*-2-butene) following zero-order reaction kinetics. In agreement with mechanistic studies of this reaction [19,20], all three butenes are primary products, with the thermodynamically least stable isomer (1-butene) surprisingly being the main product. However, after complete consumption of 1,3-butadiene (after ∼75–110 min), adsorption sites initially blocked by 1,3-butadiene are again available and allow the readsorption of butenes, which are then hydrogenated to *n*-butane. This can be clearly seen in both figures, showing that the 1-butene concentration exhibits a maximum when 1,3-butadiene is fully consumed and then starts to decrease. The decrease in 1-butene is accompanied by an increase of *trans*/*cis*-2-butene and *n*-butane. This observation is in agreement with the existence of two reaction pathways for the 1-butene consumption, that is, isomerization to *trans*- and *cis*-2-butene and hydrogenation to *n*-butane. This can be clearly observed for Pd(110), whereas for the close-packed Pd(111) surface 1-butene consumption is faster and gives rise to mainly *n*-butane through hydrogenation. This higher selectivity of Pd(110) for butenes is reflected by the low *n*-butane yield after 6 h reaction time [16% for Pd(110) vs. 44% for Pd(111)]. Initial catalytic activities at 298 K are 8.6 and 9.8 s^{-1} for Pd(111) and Pd(110), respectively (Table 1). At higher temperature (373 K), hydrogenation reactions are favored, with 1,3-butadiene being consumed already after a few minutes [cf. Fig. 3a for Pd(110)]. As mentioned earlier, the three butenes are primary products but the rapid butadiene consumption allows the readsorption of 1-butene already in the first minutes of the reaction, producing an increased amount of *trans*-2-butene, *cis*-2-butene, and *n*-butane. Furthermore, the rapid consumption of 1-butene at 373 K creates free adsorption sites where *trans*/*cis*-2-butene readsorb and are hydrogenated to *n*-butane. In fact, after 6 h of reaction the (full) hydrogenation product *n*-butane is the main product for both catalysts. These results clearly show that both hydrogenation and isomerization are favored at higher reaction temperature, although the former is predominant. At 373 K, Pd(111) and Pd(110) exhibit markedly different catalytic activities [180 s^{-1} for Pd(110) and 38 s^{-1} for Pd(111); Table 1]. The ≈4–5 times higher activity on the more open (110) surface at high temperature agrees with previous observations [14] and can be correlated with a higher sticking probability and adsorption energy of H_2 [21] and/or with a higher hydrogen accessibility on the more open (110) surface.

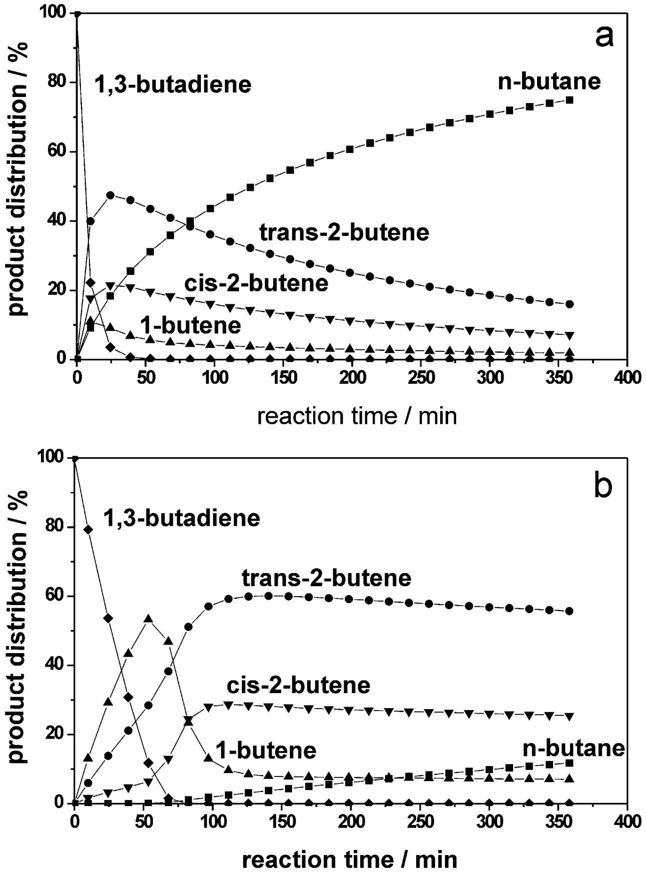

Fig. 3. Product distribution versus reaction time for the selective hydrogenation of 1,3-butadiene on Pd(110) at 373 K in (a) absence of CO and (b) presence of 0.05 mbar (50 ppm) CO.

Table 1
Selectivity of Pd(111) and Pd(110) surfaces in the selective hydrogenation of 1,3-butadiene at 298 K and 373 K for 75–80% butadiene conversion. Catalytic activity is compared based on initial turnover frequencies

Catalyst	*T* (K)	Selectivity (%)				$\frac{\text{Butene}}{\text{Butene+butane}}$	*trans*/*cis* ratio	TOF (s^{-1})
		1-Butene	*trans*-2-Butene	*cis*-2-Butene	*n*-Butane			
Pd(111)	298	49.9	33.2	9.2	7.7	92.3	3.6	8.6
	373	34.0	39.5	18.1	8.4	91.6	2.2	38
Pd(110)	298	56.5	32.2	7.5	3.8	96.2	4.3	9.8
	373	14.1	51.3	22.8	11.8	88.2	2.2	180

Density functional theory (DFT) calculations on Pd(111) have shown that at high hydrocarbon coverage the heat of adsorption changes in the order 1,3-butadiene $\gg$ 1-butene $>$ *cis*-2-butene $>$ *trans*-2-butene [22]. Considering this tendency, a high surface coverage of 1,3-butadiene is expected in the first minutes of the reaction. The higher heat of adsorption of 1,3-butadiene prevents the readsorption of the different butenes until the 1,3-butadiene surface concentration is sufficiently low to allow the readsorption of 1-butene. According to our results, low reaction temperatures and short contact times are required to obtain a high selectivity toward butenes[2]. The apparent activation energy is 36 and 25 $\mathrm{kJ\,mol^{-1}}$ for Pd(110) and Pd(111), respectively, values that are slightly smaller than those reported for Pt single crystals (39 $\mathrm{kJ\,mol^{-1}}$) [23,24]. It is also interesting to note that all activation energies obtained on single-crystal surfaces were typically smaller than those measured on supported catalysts (80 $\mathrm{kJ\,mol^{-1}}$) [25].

3.2. Effect of CO addition

For the selective hydrogenation of acetylene (HC≡CH) to ethylene ($H_2C{=}CH_2$) in an excess of ethylene (which is a key process in cleaning up polymerization streams), traces of CO are known to suppress ethylene hydrogenation to ethane (C_2H_6) on Pd catalysts [26]. To examine a possible effect of CO on the selective hydrogenation of 1,3-butadiene, the reaction was also carried out with small amounts of CO added to the reaction mixture. Fig. 3 shows the reaction kinetics on Pd(110) at 373 K for a mixture of 5 mbar C_4H_6, 10 mbar H_2, in the absence (a) and in the presence (b) of 0.05 mbar CO ($P_{C_4H_6}/P_{CO} = 100$; with Ar added to 1 bar). When Figs. 3a and b are compared, it is apparent that adding only 0.005% (50 ppm) CO to the reaction mixture induced pronounced changes in the product distribution, the most important effect being a strong reduction in n-butane formation. CO decreased the rate (TOF) of 1,3-butadiene hydrogenation from 180 to 14 s^{-1}, which is also evident from the presence of diene after 60 min (whereas in the absence of CO, the diene is consumed in the first minutes). However, there is no formation of n-butane in the presence of 1,3-butadiene. The readsorption of 1-butene is not restricted in the presence of CO, as is evident from the rather rapid 1-butene consumption, but it seems that mainly isomerization and hardly any hydrogenation occurs. Apparently, traces of CO completely suppress the hydrogenation of 1-butene to n-butane without affecting the adsorption of 1,3-butadiene and 1-butene. It is very likely that readsorption of *trans*- and *cis*-2-butene also occurs, but their hydrogenation is very slow. In fact, after 6 h of reaction, the concentration of n-butane is $<12\%$, a value six times smaller than that for the same reaction in the absence of CO (75%).

As mentioned earlier, previous studies on selective acetylene hydrogenation on Pd indicated that CO traces increased the selectivity to ethylene but an exact reaction mechanism has not yet been established. Park et al. [26] studied the effect of CO on acetylene and ethylene hydrogenation on Pd/Al_2O_3 by deuterium tracer studies. For C_2H_2 hydrogenation, these authors showed that adsorbed CO displaces surface hydrogen and thus decreases the hydrogenation probability for the adsorbed vinyl ($–C{=}CH_2$) species. This is supported by previous studies reporting that adsorbed CO strongly limits hydrogen adsorption on Pd single crystals and Pd nanoparticles [27–29]. For C_2H_4 hydrogenation on Pd/Al_2O_3, Park et al. [26] observed that CO addition displaces ethylene, favoring its desorption without any further reaction, in accordance with CO-C_2H_4 coadsorption studies on Pt(111) single crystals [30,31]. Similarly, McGown et al. also suggested a preferential adsorption of carbon monoxide (compared with ethylene) on Pd/Al_2O_3 to explain the enhanced selectivity to C_2H_4 [32].

As shown earlier, our experimental results on 1,3-butadiene clearly indicate suppression of hydrogenation in the presence of coadsorbed CO. However, adsorbed CO has a smaller effect on the adsorption of 1,3-butadiene and 1-butene, because both species are consumed during the reaction (Fig. 3b). Taking into account these results and considering previous observations, two effects may be responsible for the CO-induced changes in selectivity: (i) adsorbed CO may strongly limit H_2 adsorption on Pd(110) and to some extent hydrocarbon adsorption in general, or (ii) CO may selectively poison those surface sites that are required for (full) hydrogenation.

Increasing the amount of CO in the reaction mixture to 0.05% (500 ppm) (0.5 mbar CO; $P_{C_4H_6}/P_{CO} = 10$) resulted in complete inhibition of the hydrogenation reaction, the n-butane yield being only $\sim$2% after 6 h (not shown). The final concentration of the other reaction products was 61% *trans*-2-butene, 29% *cis*-2-butene, 8% 1-butene, and 0% 1,3-butadiene, giving rise to a nearly 100% selectivity to butenes. The absence of 1,3-butadiene and the low concentration of 1-butene clearly shows that the presence of CO has no detrimental effect on 1,3-butadiene hydrogenation and on 1-butene isomerization but completely suppresses the hydrogenation of butenes to n-butane. Under these conditions, the TOF is as low as 7 s^{-1}.

To further elucidate the effect of CO, we have also studied the hydrogenation of 1-butene at 373 K (5 mbar C_4H_8, 10 mbar H_2, Ar added to 1 bar), with and without CO addition (Figs. 4a and b). In the absence of CO, both isomerization and hydrogenation took place within the first minutes with a product distribution of 33% *trans*-2-butene, 15% *cis*-2-butene, and 52% n-butane. The complete consumption of 1-butene then produced free adsorption sites that allowed *trans*- and *cis*-2-butene readsorption and hydrogenation to n-butane. In fact, after 4 h, $\sim$100% n-butane

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[2] For completeness, we mention that the behaviour of Pd single-crystals somewhat differs from that of platinum single-crystals [23] and supported platinum [25] for which the selectivity towards butenes increased with reaction temperature.

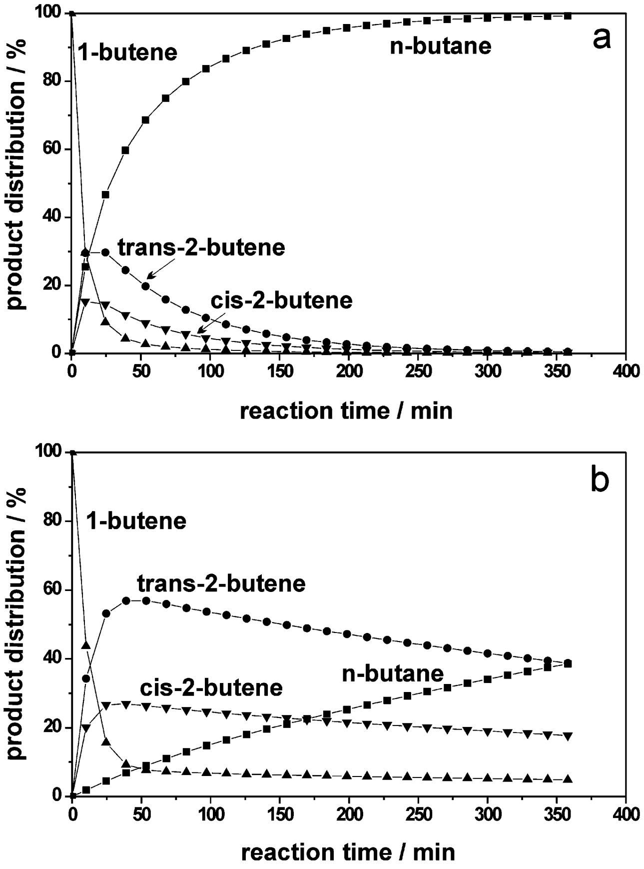

Fig. 4. Product distribution versus reaction time for 1-butene hydrogenation on Pd(110) at 373 K in (a) absence of CO and (b) presence of 0.05 mbar (50 ppm) CO.

was obtained. This behavior is in good agreement with that observed for 1,3-butadiene (Fig. 3a), where hydrogenation was favored at high temperature and long reaction times. Addition of 50 ppm CO to the reaction mixture again suppressed 1-butene hydrogenation, finally producing 41% *trans*-2-butene, 19% *cis*-2-butene, and 40% *n*-butane after 6 h (whereas *n*-butane was the only product in the absence of CO). Again, this result agrees well with the catalytic behavior observed for 1,3-butadiene hydrogenation in the presence of CO.

As discussed earlier, CO-induced suppression of the hydrogenation reaction must be related to displacement of hydrogen by CO or/and to a selective blocking of the active sites for hydrogenation, but without affecting hydrocarbon adsorption and isomerization. Once again, it is important to note that only the hydrogenation of the butenes to *n*-butane is suppressed, whereas 1,3-butadiene hydrogenation to 1-butene and 1-butene isomerization are nearly unaffected.

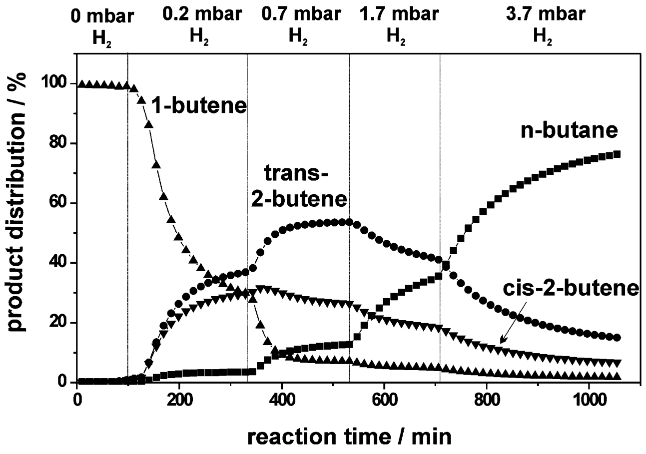

Fig. 5. Product distribution of 1-butene hydrogenation on Pd(110) at 373 K as a function of H_2 pressure.

One could argue that this effect is due simply to the total blocking of hydrogen adsorption by CO, which would strongly favor isomerization. However, as we discuss later in this paper, adsorbed hydrogen is also required for isomerization. To examine the role of hydrogen, we have carried out kinetic measurements of 1-butene isomerization and hydrogenation for different hydrogen concentrations. Fig. 5 shows the evolution of reaction products at 373 K for increasing H_2 pressure. In the absence of H_2, 1-butene hydrogenation was (of course) not observed (indicating that self-hydrogenation is negligible), but isomerization also did not occur. But adding only 0.2 mbar H_2 ($P_{C_4H_8}/P_{H_2} = 25$) resulted in a sudden decrease of 1-butene (conversion ~70% after 3 h). Interestingly, under these conditions, isomerization mainly to *trans*- and *cis*-2-butene took place with an *n*-butane fraction <3%. It is also noteworthy that the final trans/cis ratio was 1.2 under H_2-deficient conditions. An increase in the H_2 pressure to 0.7 mbar resulted in further 1-butene consumption, down to 7%. However, the higher H_2 concentration also increased the amount of *n*-butane, and also favored the formation of *trans*-2-butene as compared with *cis*-2-butene in the isomerization process (*trans*/*cis* = 2.1). Most likely, the low concentration of 1-butene favored the readsorption of *cis*-2-butene, which was hydrogenated to *n*-butane. Higher H_2 concentrations (2–4 mbar) promoted the hydrogenation reaction through the readsorption and hydrogenation of both *trans*- and *cis*-2-butene. The final product distribution obtained at high H_2 concentration after 6 h was quite similar to that discussed earlier for 1,3-butadiene hydrogenation and 1-butene hydrogenation (cf. Figs. 3a and 4a).

According to these results, there is a critical hydrogen concentration that governs reaction selectivity. Below the critical H_2 pressure, isomerization is the only process, whereas above the critical pressure, both isomerization and hydrogenation take place. If the H_2 pressure is much higher than the critical value, then hydrogenation dominates. This picture is supported by previous observations of 1,3-butadiene hydrogenation on Pd/Al_2O_3 and Pd–Cu/Al_2O_3 [9].

Similar experiments (with and without CO) were performed for the hydrogenation of 1,3-butadiene on Pd(111) at 373 K. As mentioned earlier, in the absence of CO and at 373 K, Pd(111) exhibits a catalytic activity (TOF) of 38 s^{-1}, with *n*-butane being the main product after 6 h on stream (55%). Addition of 0.05 mbar (50 ppm) CO drastically re-

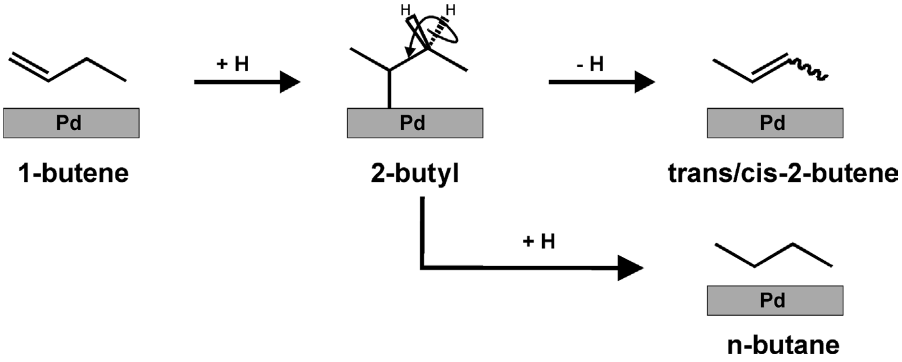

Fig. 6. Reaction scheme proposed for 1-butene isomerization and hydrogenation.

duced the catalytic activity (TOF 1 s^{-1}), with a butadiene conversion after 10 h reaction time of still 64%. CO addition certainly inhibits hydrogen adsorption on the Pd(111) surface [28], but some blocking of hydrocarbon adsorption is also very likely. On the more open Pd(110) surface, the presence of ridges and troughs seems crucial to avoid the complete poisoning of the catalyst, which may explain the differences in activity between Pd(110) and Pd(111).

3.3. Reaction mechanism

Nuclear extended X-ray absorption studies of 1,3-butadiene and 1-butene chemisorption on Pd single-crystal surfaces have shown that both molecules are physisorbed at 95 K. At higher temperature (300 K), 1,3-butadiene adsorbs in a di-π mode on different Pd surfaces, whereas 1-butene tends to dehydrogenate to butadiene on Pd(110) [15,16]. This result differs from DFT calculations on Pd(111), where a tetra-σ adsorption mode of 1,3-butadiene was suggested to be the most stable [22]. Considering a di-π adsorption of 1,3-butadiene on Pd(111) and Pd(110), the first step in the hydrogenation reaction would be the addition of a H atom to one of the two equivalent double bonds ($C_1{=}C_2$ or $C_3{=}C_4$). Because the two carbon atoms of the same double bond are not equivalent, the position of the H addition defines the final regioselectivity. Hydrogen addition to a terminal carbon (C_1 or C_4) produces 2-butenyl species, whereas H addition to an internal carbon (C_2 or C_3) produces a 1-butenyl intermediate. Infrared-visible sum-frequency generation (SFG) spectroscopy of atmospheric-pressure propylene hydrogenation on Pt(111) at 295 K (40 Torr propylene, 723 Torr H_2) detected mainly 2-propyl [33], suggesting H addition to a terminal carbon as the preferred reaction pathway.

Once the 2-butenyl group is formed, the molecule can be further hydrogenated at the adjoining carbon (C_2) to 1-butene (1,2-hydrogen addition), or 2-butenyl can be hydrogenated at the other terminal carbon (C_4), giving rise to 2-butene isomers (1,4-hydrogen addition). Consequently, the probability of hydrogen addition to C_2 or C_4 atoms will define the final distribution of butenes. If both additions have the same probability, then a 1-butene:2-butene ratio of 1:1 is expected, with the relative yield of *trans*- and *cis*-2-butene being defined by the conformational characteristics (*syn*/*anti*) of the adsorbed precursor. Because we do not observe a significantly higher amount of 1-butene, we can confirm that 1,3-butadiene is adsorbed with both double bonds. Otherwise, if the second double bond were away from the surface and unavailable for hydrogenation, then an increased fraction of 1-butene should occur via 1,2-addition.

After the three butenes were formed (and 1,3-butadiene was consumed), experiments showed that the readsorption of mainly 1-butene gave rise to isomerization to *trans*- and *cis*-2-butene, as well as hydrogenation to n-butane. The preferential adsorption of 1-butene on Pd surfaces correlates with calculations proposing the adsorption of 1-butene to be 13 $kJ\,mol^{-1}$ more stable than adsorption of *cis*-2-butene and 18 $kJ\,mol^{-1}$ more stable than adsorption of *trans*-2-butene adsorption [22]. Similar to 1,3-butadiene, π-adsorbed 1-butene is hydrogenated at the terminal carbon, producing 2-butyl intermediates. The 2-butyl group can then be further hydrogenated to n-butane or can lose β-H to produce the 2-butenes [34].

The proposed reaction mechanism (i.e., hydrogen addition to form 2-butyl and subsequent β-H elimination) is well accepted for butene isomerization, but an alternative (reverse) reaction pathway has been proposed for *cis*-2-butene isomerization on Pt catalysts [35]. This pathway involves the dissociative adsorption of *cis*-2-butene as 2-butyne [36], followed by H addition to the dehydrogenated intermediate to yield *trans*-2-butene. Our measurements clearly show that both 1-butene hydrogenation and isomerization occur only in the presence of H_2. This indicates that the first step in both processes is the addition of H to create an alkyl intermediate, supporting the first reaction mechanism (see Fig. 6).

Whereas the isomerization reaction proceeds via β-H elimination within the alkyl intermediate (i.e., without a “second” hydrogen atom), hydrogenation to n-butane requires another “extra” hydrogen addition. Apparently, small H coverage is sufficient to create the 2-butyl intermediates involved in both reactions, but a small amount of surface H still favors isomerization to *trans*/*cis*-2-butene. It is worth mentioning that the hydrogen produced by β-elimination is again available for the formation of another 2-butyl group. This explains how the addition of only 0.2 mbar H_2 is able to isomerize 3.5 mbar 1-butene in <2 h. In agreement with the first reaction mechanism, increasing the hydrogen pressure produces a higher H surface concentration, which allows hydrogenation of 2-butyl intermediates to n-butane.

As discussed earlier, on open Pd(110) surfaces, coadsorbed CO decreases the hydrogen surface concentration to a critical value that does not affect 1,3-butadiene hydrogenation to butenes and 1-butene isomerization to *trans*/*cis*-2-butene but that prevents butene hydrogenation. For 1,3-butadiene, the only possible reaction process is hydrogenation, and thus the only effect of CO is decreased hydrogenation activity, as observed experimentally. However, on close-packed (111) surfaces, the blocking effect of CO is much stronger, as evidenced by the drastic inhibition of catalytic activity. Apparently, CO almost completely inhibits hydrogen adsorption, although effects on butadiene adsorption also are likely.

Previous studies of high-pressure CO adsorption on Pd(111) by SFG and X-ray photoelectron spectroscopy indicated a CO surface coverage of $\sim$0.5 ML between 300 and 400 K, for a CO pressure of 5×10^{-3} mbar CO. At 1 mbar CO, $\sim$0.6 ML CO were observed in the same temperature range [37]. A similar increase in CO coverage may be responsible for the more detrimental effect on the hydrogenation activity after increasing the CO pressure from 0.05 to 0.5 mbar. According to these results, and considering a similar surface CO coverage on Pd(111) and Pd(110), the presence of ridges and troughs on the more open (110) surface seems critical to allow hydrogen dissociation and reaction.

In our experiments, the hydrogen pressure was selected such to avoid the formation of β-Pd-hydride, which would lead to recrystallization of the Pd single crystals (and thereby destroy their well-defined surface structure). Nevertheless, hydrogen can easily dissolve in Pd at the reaction temperature of 373 K, and involvement of dissolved hydrogen in the catalytic reaction [28,29,38–42] (by, e.g., supplying H to the surface) cannot be ruled out, even though the probability of hydrogen dissolution seems small in light of the high reaction rate and the presence of a blocking hydrocarbon overlayer.

4. Conclusions

The selective hydrogenation of 1,3-butadiene has been studied at atmospheric pressure on Pd(111) and Pd(110) single crystals. Based on the catalytic measurements, we can draw the following conclusions:

1. Kinetic measurements (catalytic activity and selectivity) on Pd(110) and Pd(111) confirmed that the selective hydrogenation of 1,3-butadiene on Pd catalysts is a structure-sensitive reaction [14].
2. In the initial stages of the reaction, 1,3-butadiene is the only adsorbed species producing 1-butene, *trans*-2-butene, and *cis*-2-butene as primary reaction products. Once 1,3-butadiene is consumed, 1-butene is readsorbed and reacts to *trans*/*cis*-2-butene through isomerization and to n-butane through hydrogenation.
3. On Pd(111), 1-butene readsorption after complete 1,3-butadiene consumption leads mainly to hydrogenation to n-butane, whereas on Pd(110), both isomerization to *trans*/*cis*-2-butene and hydrogenation to n-butane occur. This reflects the higher selectivity of Pd(110) toward butene formation.
4. Kinetic measurements of 1-butene hydrogenation at different H_2 pressures show that the selectivity is determined by the surface hydrogen concentration. For instance, at supposedly low hydrogen coverage, isomerization is the main reaction process, whereas at high H_2 coverage and long reaction time, hydrogenation to n-butane is favored. In the absence of hydrogen, no reaction (not even isomerization) occurs.
5. The addition of small amounts of CO drastically inhibits catalytic activity of Pd(111). In contrast, the addition of CO to Pd(110) inhibits the (secondary) hydrogenation of 1-butene to n-butane without affecting 1,3-butadiene hydrogenation and 1-butene isomerization. Apparently, CO addition decreases the hydrogen concentration to a critical coverage that is still sufficient for 1-butene isomerization but not for its hydrogenation. For 1,3-butadiene, only hydrogenation is possible, and the only effect of CO is to decrease the activity.
6. The detrimental effect of CO on the close-packed Pd(111) surface points to the important role of ridges and troughs on the more open Pd(110) surface for hydrogenation reactions. This may explain the higher activity of Pd(110) as compared to Pd(111).

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