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Conversion of *cis*- and *trans*-2-butene with Deuterium on a Pd/Fe_3O_4 model catalyst

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ABSTRACT

Combining molecular beam (MB) techniques, reflection–absorption infrared spectroscopy (RAIRS), and temperature-programmed desorption (TPD), we have investigated the adsorption and kinetics of conversion of *cis*- and *trans*-2-butene with deuterium on a well-defined model supported Pd catalyst. Particular emphasis was placed on the quantitative comparison of the reaction rates of the competing *cis-trans* isomerization and hydrogenation pathways between both steric isomers. It was observed that the reaction temperature critically affects the *cis-trans* selectivity of 2-butene in both reaction paths. At low-temperatures (195–210 K), *cis*-2-butene shows higher activity toward both hydrogenation and isomerization reactions han the *trans* isomer. At temperatures above 250 K, on the other hand, very similar reaction rates were found for both isomers. Remarkably, deposition of sub-monolayer amounts of strongly dehydrogenated carbonaceous species on the Pd particles results in a significant decrease of the *cis-trans* isomerization rate for *trans*-2-butene, but does not affect the rate of this pathway for the *cis* isomer. Additionally, under high-temperature conditions (250–260 K), co-deposited carbon was shown to assist the catalytic and sustained hydrogenation of both *cis*- and *trans*-2-butene, both at similar rates.

1. Introduction

Tuning selectivity in hydrocarbon conversions toward desirable reaction pathway is one of the major tasks in catalysis research, and is essential for many industrial processes [1–3]. In particular, controlling selectivity in the formation of *cis*- vs. *trans*-olefins has a significant practical importance for the production of *cis* fatty unsaturated acids during the partial hydrogenation of natural edible oils [4,5]. Although conventional catalytic studies [6–8] and more modern surface-science work [9–11] have provided much insight into the microscopic details of hydrocarbon conversions, a detailed understanding of the phenomena controlling *cis-trans* selectivity is still not available [12,13].

In the past, it has been difficult to test selectivity in carbon–carbon double bond isomerizations using traditional surface-science techniques because many of them are not suitable to discriminate between *cis* and *trans* isomers [14], but Lee and Zaera have recently developed an approach to overcome this limitation via the use of H–D exchange reactions as proxies for *cis-trans* isomerizations [15]. Interestingly, they found that isomerization of *trans*-2-butene to its *cis* counterpart is easier than the opposite *cis*-to-*trans* isomerization on Pt(1 1 1) surfaces [15–17]. This unusual catalytic behavior [18–22], resulting in the formation of the thermodynamically less stable gas phase product – *cis*-2-butene – at a significantly faster rate, was ascribed to differences in the stability of *cis*- and *trans*-isomers on the closed-packed (1 1 1) plane [23]. Based on these considerations, it was predicted that the structure of the catalytic surface should have a pronounced effect on *cis-trans* transformations [23,24]. Evidence for this using shape-controlled catalysts has in fact been acquired recently for platinum [24,25].

To test the generality of the preceding conclusion to other metals, in this report we present a comprehensive study on the relative stability and reactivity of *cis*- vs. *trans*-2-butene on a realistic model catalytic surface consisting of supported palladium nanoparticles grown *in situ* on a planar Fe_3O_4/Pt(1 1 1) thin film under ultra high vacuum (UHV) conditions. Such well-defined, oxide-supported catalyst is simple enough to allow for a detailed characterization of their microscopic structure by a variety of surface-science techniques, yet sufficiently complex to still mimic specific important features of real catalysts [26–30]. We applied a combination of molecular beam methods, TPD, and reflection–absorption infrared spectroscopy (RAIRS) [31] to obtain detailed information on the stability and reactivity of 2-butenes on these supported Pd nanoparticles.

Particular emphasis is placed on a quantitative comparison between the reactivity of the two conformational isomers of 2-butene – *cis* and *trans* – in competing *cis-trans* isomerization and hydrogenation reaction pathways. Recent work in our

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laboratory on the conversion of *cis*-2-butene with deuterium on this model catalyst has led to the conclusion that the activity and selectivity toward *cis-trans* isomerization and hydrogenation critically depend on the presence of dehydrogenated carbonaceous deposits resulting from decomposition of the reactants [32–34]. In this study, we evaluate the role of such carbonaceous species in the *cis*- vs. *trans*-2-butene conversions. Two different temperature reaction regimes were found: a low-temperature range, below approximately 220 K, where *cis*-2-butene shows a significantly higher reactivity in both *cis-trans* isomerization and hydrogenation reactions than its *trans*-counterpart, and a higher-temperature regime, above ∼250 K, where very similar reaction rates are measured for both conformational isomers. The presence of strongly dehydrogenated carbonaceous species on the surface was found to affect the reactivity of *cis*- and *trans*-2-butene and their selectivity toward *cis-trans* isomerization and hydrogenation in significantly different ways. Possible molecular-level explanations for these phenomena based on the kinetic data are discussed.

2. Experimental

All molecular beam (MB), TPD, and RAIRS experiments were performed at the Fritz–Haber-Institut (Berlin) in a UHV apparatus described in detail previously [31]. Briefly, two molecular beams, of D_2 and either *cis*- or *trans*-2-butene, were crossed on the sample surface. An effusive doubly differentially pumped multi-channel array source was used to supply the D_2, modulated using remote-controlled shutters and valves. Beam intensities for D_2 of 3.2×10^{15} molecules $cm^{-2}\,s^{-1}$ were used in these experiments. The source was operated at room temperature, and the beam diameter was chosen such that it exceeded the sample diameter. A supersonic beam, generated by a triply differentially pumped source and modulated by a solenoid valve and a remote-controlled shutter, was used to dose the *cis* and *trans*-2-butenes (Aldrich, >99%) at an intensity of 5.6×10^{12} molecules $cm^{-2}\,s^{-1}$ (typical backing pressure: 1.15 bar). The diameter of this beam was chosen to be smaller than that of the sample for the experiments discussed here. An automated quadrupole mass spectrometer (QMS) system (ABB Extrel) was employed for the continuous and simultaneous monitoring of the partial pressures of the reactants (2-butene, followed by the signal of the $C_3H_5^+$ fragment at 41 a.m.u. because of experimental reasons) and products (2-butene-d_1, $C_3H_4D^+$ fragment at 42 a.m.u.; 2-butene-d_2, $C_3H_3D_2^+$ fragment at 43 a.m.u.; butane-d_2, $C_3H_5D_2^+$ fragment at 45 a.m.u., and butane-d_3, $C_3H_4D_3^+$ fragment at 46 a.m.u.). All QMS data have been corrected to account for the natural abundance of ^{13}C in the hydrocarbons. TPD experiments were carried out in the same vacuum system and by using the same QMS instrumentation. Linear heating ramps for the sample were set to a value of $3.5\ K\,s^{-1}$. RAIRS data were acquired by using a vacuum Fourier-Transform Infrared (FT-IR) spectrometer (Bruker IFS 66v/S) with a spectral resolution of $2\ cm^{-1}$ and using a mid-infrared (MIR) polarizer and p-polarized IR light.

The Pd/Fe_3O_4 model catalyst was prepared as follows: the thin (∼100 Å) Fe_3O_4 film was grown on a Pt(1 1 1) single crystal surface by repeated cycles of Fe (>99.99%, Goodfellow) physical vapor deposition and subsequent oxidation (see [35–38] for details). The cleanliness and quality of the oxide film were checked by RAIRS of adsorbed CO and by LEED. Pd particles (>99.9%, Goodfellow) were then grown on this film by physical vapor deposition using a commercial evaporator (Focus, EFM 3, flux calibrated by a quartz microbalance) while keeping the sample temperature fixed at 115 K. During Pd evaporation, the sample was biased in order to avoid the creation of defects by metal ions. The final Pd coverage used in these experiments was 2.7×10^{15} atoms cm^{-2}. Finally, the resulting surfaces were annealed to 600 K, and stabilized via a few cycles of oxygen (8×10^{-7} mbar for 1000 s) and CO (8×10^{-7} mbar for 3000 s) exposures at 500 K before use [38]. An STM image of the model surface resulting from this preparation is shown in Fig. 1. This surface displays Pd particles with an average diameter of 7 nm containing approximately 3000 atoms each, and covering the support uniformly with an island density of about 8.3×10^{11} islands cm^{-2} [38]. The majority of the particles

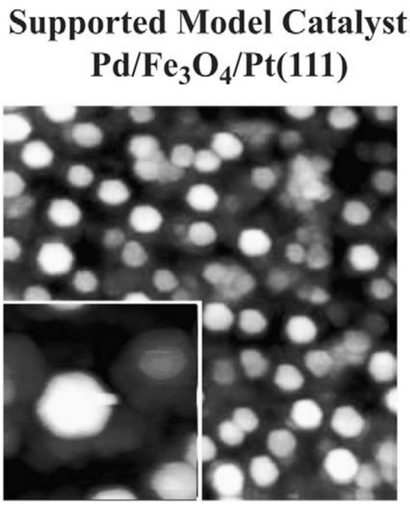

Fig. 1. Scanning tunnelling microscopy (STM) image (100 nm × 100 nm, inset: 20 nm × 20 nm) of the $Pd/Fe_3O_4/Pt(1\,1\,1)$-supported model catalyst used in the experiments. The Pd particles exhibit mostly (1 1 1) facets (the top and three of side facets) and smaller fraction of the (1 0 0) facets (three side facets).

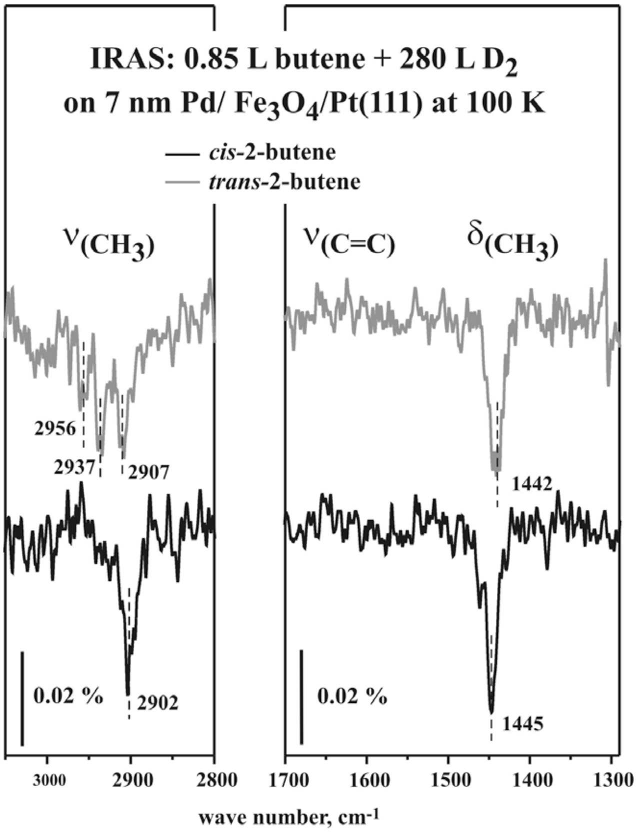

Fig. 2. RAIR spectra for the $Pd/Fe_3O_4/Pt(1\,1\,1)$ catalyst after sequentially dosing 280 L of deuterium and 0.85 L of cis- (black traces) and *trans*-2-butene (gray traces) at 100 K.

are well-shaped crystallites grown in the (1 1 1) orientation, and are predominantly terminated by (1 1 1) facets (~80%), but a small fraction of (1 0 0) facets (~20%) is also exposed.

For carbon deposition, 0.85 Langmuir (1 L = 10^{-6} Torr s) of 2-butene was adsorbed on the Pd clusters pre-exposed to 280 L of D_2 at 100 K and decomposed by heating to 485 K (see [32] for details).

3. Results and discussion

3.1. cis- and trans-2-butene adsorption on Pd/Fe_3O_4: RAIRS

First, the adsorption of *cis*- and *trans*-2-butenes on the supported Pd nanoparticles was investigated and compared by RAIRS. Fig. 2 shows the RAIRS data obtained after sequential exposures of the Pd/Fe_3O_4 surface to 280 L of D_2 and 0.85 L exposures of either *cis*- or *trans*-2-butene at 100 K; these exposures were chosen to assure near saturation of the surface with deuterium and molecular butene. Four main absorption bands are seen in the spectrum of *trans*-2-butene: two at 1445 and 2907 cm^{-1}, corresponding to the fundamental and first overtone mode of the asymmetric deformation of the terminal methyl moieties ($\delta_{as}(CH_3)$), also visible in the data for the *cis* isomer [32], and two distinctly resolved vibrational bands at 2937 and 2956 cm^{-1} associated with asymmetric C–H stretching modes ($\nu_{as}(CH_3)$) [39–41]. The frequencies of all these modes are quite close to those seen for *trans*-2-butene in the gas phase, implying minimal molecular distortion upon adsorption (most likely via π bonding), but the fact that the latter two C–H asymmetric stretching modes are not seen in the RAIRS spectra of the *cis*-2-butene suggests a different adsorption geometry for the two isomers. Also worth noting is the absence of any signal for the vibrational band at around 1660 cm^{-1} corresponding to the C=C stretching mode, $\nu(C{=}C)$, which, based on the selection rule that applies to infrared absorptions on metal surfaces [42,43], hints at an adsorption with the C=C double bond parallel to the surface. Note that the applicability of the metal surface selection rule is ensured by the presence of both the planar extended Pt(1 1 1) substrate underlying the oxide film and the metal nanoparticles. It should be noted that π bonding, as seen here, is known to dominate on hydrogen (or deuterium)-predosed platinum surfaces [44], even if some rehybridization is still seen on the clean surface of that metal [16].

3.2. cis- and trans-2-butene conversion on Pd/Fe_3O_4 in the presence of coadsorbed deuterium: TPD

The surface chemistry of both *cis* and *trans* 2-butene on the Pd particles pre-saturated with deuterium was investigated next. Fig. 3 displays the TPD spectra obtained after dosing 0.85 L of either alkene on the Pd particles pretreated with 280 L of molecular deuterium at 100 K. Both *cis*- and *trans*-2-butene show a multilayer molecular desorption peak at about 145 K and a monolayer desorption feature at 185 and 173 K for the *cis* and *trans* isomers, respectively. The difference in peak temperature between the two isomers in the latter feature indicates slightly stronger

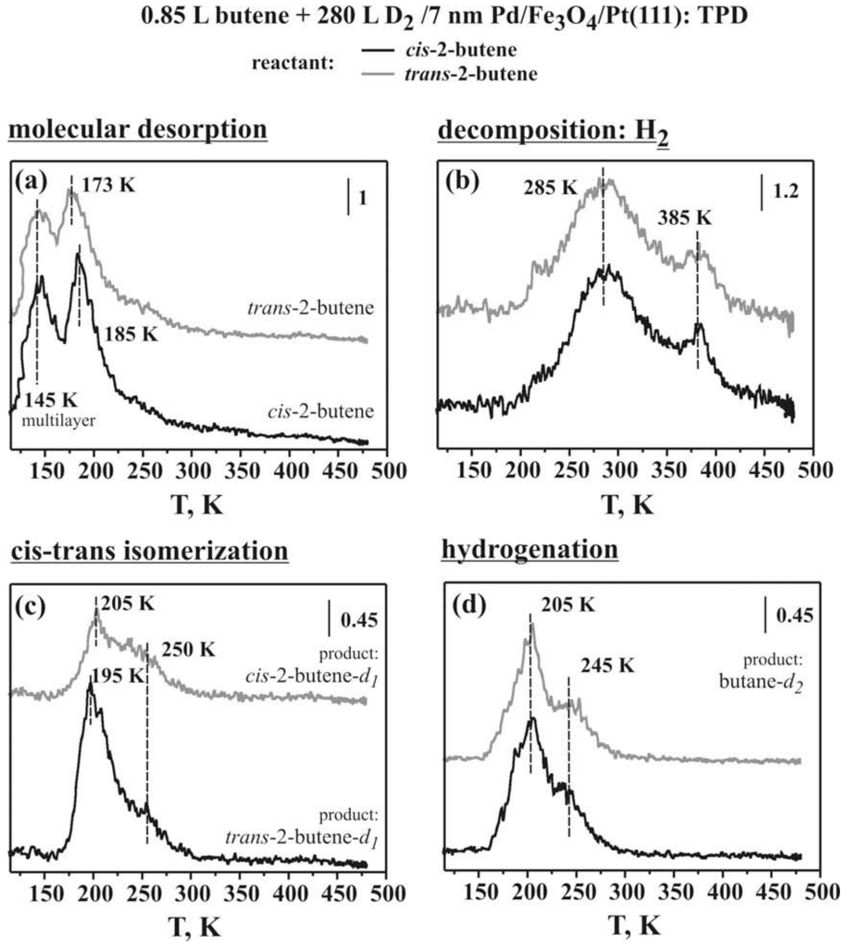

Fig. 3. TPD traces from our Pd/Fe_3O_4 model catalyst after sequential dosing of 280 L of D_2 and 0.85 L of *cis*- (black traces) and *trans*-2-butene (gray traces) at 100 K. The traces for (a) molecular desorption of the starting reactant; (b) H_2 desorption from butene dehydrogenation; (c) *trans*- and *cis*-2-butene-d_1 from isomerization of *cis*- and *trans*-2-butene, respectively; and (d) butane-d_2 from deuteration of both starting reactants are shown.

adsorption of the *cis* conformer: the adsorption energies are estimated (by using Redhead's equation [45] and a preexponential factor of $10^{15}\ s^{-1}$) at 47 and 44 kJ mol^{-1}, respectively. Higher adsorption stability for the *cis* isomer was previously observed by TPD both on pristine (that is, not hydrogen- or deuterium-pretreated) Pd particles [32,46] and on Pt(1 1 1) [15,16]. It was explained by its ability to reduce any steric repulsion between the methyl-groups and the surface via tilting of the molecular plane, hence minimizing the degree of surface reconstruction required [23,24]. On the other hand, molecular adsorption of either isomer is considerably weaker on the deuterium-precovered vs. pristine Pd/Fe_3O_4, and the absolute molecular desorption yield is about 70% larger, pointing to a lower extent of decomposition.

Hydrogen desorption from butene decomposition shows nearly identical behavior for both *cis* and *trans* isomers, and occurs in several stages peaking at 285 and 385 K (Fig. 3b). Since recombinative desorption of hydrogen atoms on the Pd particles occurs between 200 and 370 K [47], the broad feature at 285 K might be attributed either to the commencement of alkene decomposition or to the onset of recombinative desorption of the hydrogen atoms formed during butene dehydrogenation at lower temperatures. The second TPD peak at 385 K is undoubtedly limited by the rate of alkene decomposition. The nearly identical H_2 TPD traces obtained with both *cis*- and *trans*-2-butene isomers suggest dehydrogenation through the same surface intermediates. Furthermore, the general agreement between our data and reported TPD traces obtained on single crystals suggests that those intermediates are most likely di-σ bonded 2-butyne at room temperature and highly dehydrogenated carbonaceous deposits (presumably C_4H_2) above 400 K [15–17,48–53] (for more detailed discussion see [32]).

Thermal activation of 2-butenes co-adsorbed with deuterium on the supported Pd particles also leads to extensive *cis*-*trans* isomerization (Fig. 3c) and hydrogenation (deuteration) (Fig. 3d). Interestingly, whereas the TPD traces for the first reaction are significantly different for the *cis*- vs. *trans*-2-butene isomers, those for the butane-d_2 deuteration product are nearly identical with both isomers. Specifically, the production of monodeuterated *trans*-2-butene-d_1 from *cis*-2-butene peaks at 195 K and displays a small shoulder at 250 K, whereas the desorption of *cis*-2-butene-d_1 from the *trans* isomer peaks at 205 K and has a shoulder at 250 K. Also, the intensity of the first TPD desorption with the *trans* isomer is approximately a factor of 1.5 lower than that with *cis*-2-butene. Production of some doubly exchanged/doubly isomerized 2-butenes-d_2 was detected at approximately the same temperatures with both compounds, but no further H–D exchanged alkenes were seen. In terms of the deuteration reaction, the resulting butane-d_2 desorbs in a main peak at 205 K and a shoulder at 245 K with both reactants, and show nearly the same total yields in both cases.

These TPD results highlight the fact that while olefin hydrogenation displays similar kinetics with both *cis* and *trans* isomers on the Pd particles, there are some pronounced differences between the two in terms of *cis-trans* isomerization. Interestingly, the higher *cis-trans* isomerization yields observed here for the *cis* isomer are in sharp contrast to the results previously obtained in studies with both Pt(1 1 1) single crystals [15] and supported Pt tetrahedral particles [24], where the opposite trend – an easier isomerization with *trans*-2-butene – was found. The faster isomerization rate of the *trans* isomer on Pt(1 1 1) was ascribed to a higher stability of the adsorbed product (*cis*-2-butene), but a higher

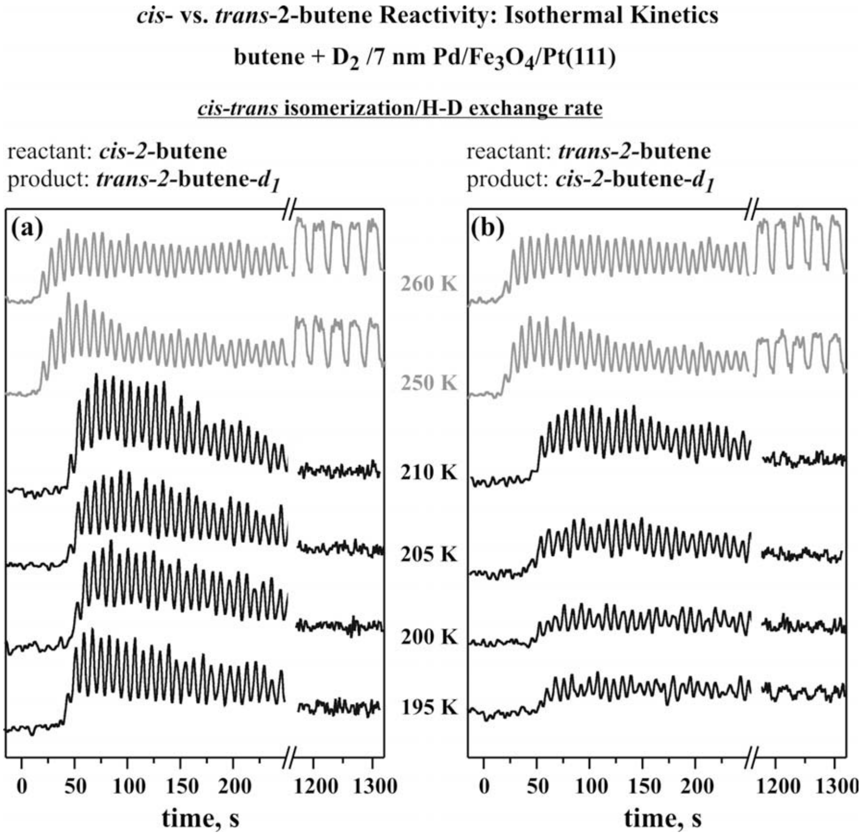

Fig. 4. Kinetics of *cis*-*trans* isomerization obtained in isothermal molecular beam experiments carried out between 195 and 260 K on an initially clean Pd/Fe_3O_4 catalyst by using the pulse scheme described in the text. The reaction rates are displayed for *cis*- ((a) product *trans*-2-butene-d_1) and *trans*-2-butene ((b) product *cis*-2-butene-d_1). *cis*-2-butene shows pronouncedly higher reactivity in the temperature range 195–210 K than the *trans* isomer, at temperatures above 250 K the differences in the reactivity between both the isomers nearly vanish.

stability of the *cis*-2-butene isomer was observed in our TPD data on Pd particles as well. Therefore, this factor alone cannot account for the observed trend on the Pd particles.

3.3. cis- and trans-2-butene conversion with deuterium on Pd/Fe$_3$O$_4$: isothermal molecular beam experiments

Isothermal molecular beam (MB) experiments were performed on the Pd/Fe$_3$O$_4$ model catalyst with both the isomers. In these experiments, the sample, which was kept at a constant temperature, was exposed continuously to a D$_2$ beam while a second 2-butene beam was switched on and off, starting after 90 s from the beginning of the D$_2$ dosing, to discriminate between reactions on the surface and signals from the background. A typical MB sequence consisted of 50 short butene pulses (4 s on, 4 s off time) followed by 30 longer pulses (20 s on, 10 s off time). Fig. 4 shows the results of the experiments carried out with each *cis* (left panel) and *trans* (right panel) isomer on an initially clean Pd sample at different temperatures in the range between 195 and 260 K.

Qualitatively, the long-term kinetic behavior of the *cis-trans* isomerization reaction was found to be similar for both the isomers but to depend strongly on the reaction temperature. A detailed discussion of this temperature dependence for *cis*-2-butene can be found in [32]. An important observation here is that although non-zero initial *cis-trans* isomerization rates are observed with both *cis*- and *trans*-2-butene over the whole temperature region investigated (195–260 K), sustained catalytic activity toward isomerization under the steady-state conditions occurs only at temperatures above 250 K. We attribute the suppression of catalytic activity at low-temperatures in steady-state to a poisoning effect by hydrocarbon (HC) species, possibly molecular butene and/or partly dehydrogenated HCs, on the dissociative adsorption of hydrogen (deuterium). Above 250 K, the overall surface concentration of HCs is likely to decrease, so dissociative deuterium adsorption can effectively proceed, and sustained catalytic activity is possible.

In terms of the quantitative comparison of *cis*- vs. *trans-2*-butene reactivity, which is the focus of this report, it can be seen that *cis-2*-butene shows systematically higher *cis-trans* isomerization rates in the low-temperature region (195–210 K) than the *trans* counterpart. However, above 250 K those differences nearly vanish, and very similar steady-state isomerization rates are reached with both the isomers. Similar (although less prominent) differences in initial reactivity are also observed for the hydrogenation (deuteration) reaction (data not shown): the product yields are somewhat lower for *trans*-2-butene in the low-temperature regime (195–210 K), and are quite similar at higher-temperatures. However, no persistent hydrogenation activity is observed on the initially clean Pd particles at any reaction temperature [32–34].

It is important to point out that *cis-trans* isomerization turns to the sustained regime and reaches its maximum reaction rates between 240 and 260 K [46]. Therefore, the observation of nearly

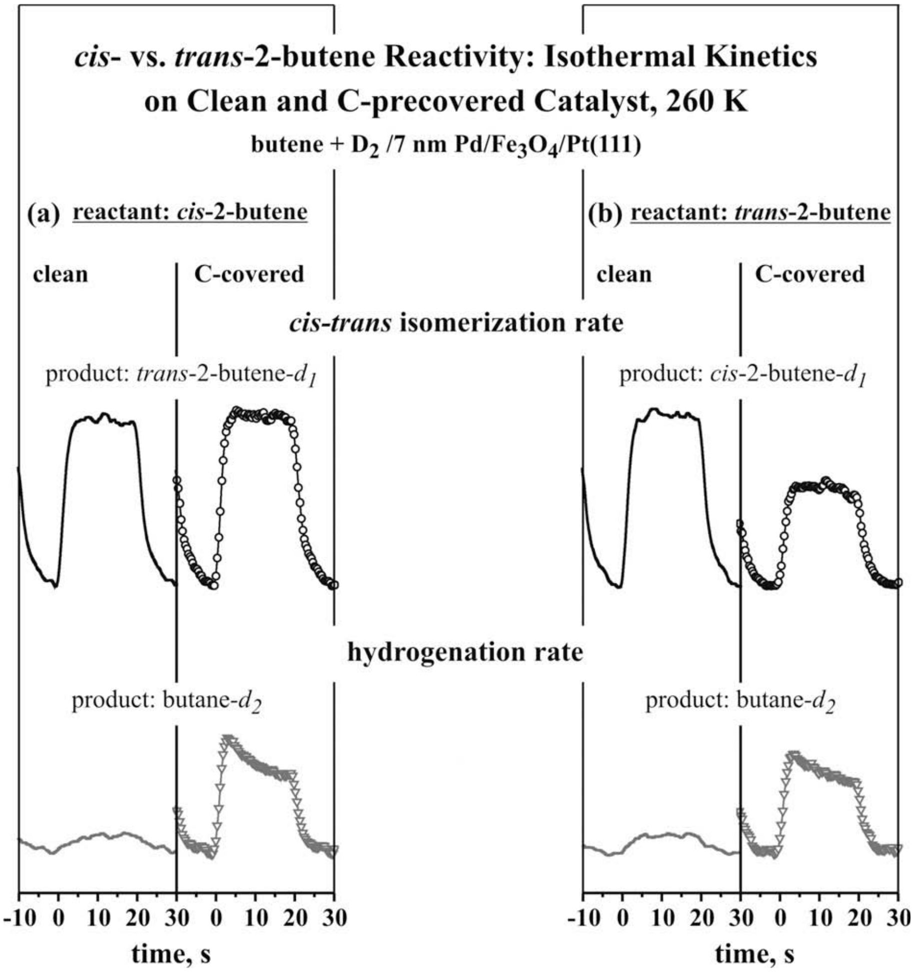

Fig. 5. Comparison of average reaction rates measured for *cis-trans* isomerization (upper row) and hydrogenation (bottom row) for *cis*- (a) and *trans*-2-butene (b) at 260 K on both initially clean and C-precovered Pd catalysts. Carbon deposition was performed according to the procedure described in the experimental section. The rates were calculated by averaging the steady-state reaction rates of the last 30 long pulses of the experiment.

vanishing differences in the *cis*- vs. *trans*-butene reactivity in this temperature regime is an important result of this study for understanding the isomerization process under catalytically relevant conditions.

3.4. *cis*- and *trans*-2-butene conversion with deuterium on Pd/Fe_3O_4: role of pre-deposited carbon

Finally, the effect of co-adsorbed strongly dehydrogenated carbonaceous species on the reactivity of *cis*- vs. *trans*-2-butene was investigated. These studies were motivated by our previous finding with *cis*-2-butene that sub-monolayer coverages of such carbonaceous deposits help maintain sustained steady-state activity for both hydrogenation and isomerization reactions with similar reaction probabilities [32–34]. Fig. 5 contrasts the results of MB experiments with *cis*- (left panel) and *trans*- (right panel) 2-butene at 260 K on initially clean (solid lines) vs. C-precovered (open symbols) catalytic surfaces. Only the steady-state reaction rates are shown, calculated by averaging the data recorded during the last 30 long pulses of the experiment.

The steady-state reaction rates for hydrogenation (deuteration) on the carbon-modified Pd particles are very similar for both *cis* and *trans* isomers. Also, as discussed above, the steady-state reaction rates of the isomerization channel are nearly identical for the *cis* and *trans* isomers on the initially clean Pd particles at 260 K. On the other hand, while the steady-state *cis-trans* isomerization rates are virtually the same on the initially clean and C-precovered Pd particles for *cis*-2-butene (left panel, upper trace, *trans*-2-butene-d_1 product), they are reduced by approximately a factor of two in the case of *trans*-2-butene (right panel, upper trace, *cis*-2-butene-d_1 product). This is so even though the amount of carbon deposited on the surface in the TPD run with *trans*-2-butene is about the same as with *cis*-2-butene, as evidenced by both the similar H_2 TPD yields seen in Fig. 3b and CO RAIRS titration experiments (data not shown). The effect of carbon deposition on the isomerization rates of *trans*- vs. *cis*-2-butene is in a good qualitative agreement with the TPD results obtained on the clean and carbon-precovered Pd particles as described in Section 3.2, in that the integrated intensity of the TPD peak on the carbon-containing species is approximately factor of two lower with the *trans* isomer.

Additionally, it is important to note that both reactions – *cis-trans* isomerization and hydrogenation – exhibit a different transient behavior upon modulation of the olefin molecular beam. All traces related to the *cis-trans* isomerization (both on the initially clean and C-covered particles) exhibit a rectangular form, suggesting that the reaction rates simply follow the time evolution of the flow of reactant in the beam. In contrast, the steady-state hydrogenation rates observed on the C-modified surfaces are high at the beginning of the butene exposure but decrease considerably over the duration of the pulse, indicating more complex kinetics. These differences were observed with both *cis* and *trans* 2-butene isomers.

3.5. Discussion

The isothermal molecular beam data discussed in the last two sections demonstrate that the differences in reactivity between *cis* and *trans* isomers of olefins on the surface of our Pd model catalyst might be induced by changes in reaction conditions and/or the chemical composition of the catalyst surface, in particular to the presence of the carbonaceous deposits that usually form under reaction conditions [3]. Specifically, here it was found that, when starting with clean Pd particles, *cis*-2-butene is more reactive than *trans*-2-butene toward both *cis-trans* isomerization and hydrogenation at low (195–210 K) temperatures, but that the difference disappears above 250 K. On the other hand, upon the addition of small amounts of carbon on the surface, the *cis* isomer exhibits a higher steady-state reactivity than its *trans* counterpart even above 250 K. It is key to note here that only the *cis-trans* isomerization reaction is affected by the co-adsorbed carbonaceous deposits; the deuteration of both the isomers proceeds with similar kinetics.

Several reasons can be invoked to explain the observed *cis-trans* selectivity in the low-temperature region and its loss under the high-temperature conditions. Starting with the low-temperature kinetics, that is between 195 and 215 K, its main characteristics are high initial rates for both *cis-trans* isomerization and hydrogenation reactions and a vanishing activity after prolonged olefin exposures (Fig. 4). As already mentioned above, the latter observation is explained by poisoning of the dissociative adsorption of deuterium molecules because of the accumulation of hydrocarbon adsorbates on the catalysts surface. In terms of the initial rates, both *cis-trans* isomerization and hydrogenation reactions are faster with *cis*-2-butene than with the *trans* isomer, but the ratio of isomerization:hydrogenation initial rates is similar for both isomers over the entire low-temperature region. This suggests that the differences in activity may be explained by the buildup of a higher surface concentration of the common reaction intermediate for both reaction pathways – butyl species [54–56] – in the case of the *cis* compared to the *trans* reactant, probably because of either a higher uptake of the more stable *cis*-butene adsorbate or an easier butyl formation starting from the *cis* adsorbate. Since there are no obvious limitations in availability for either reactant in the initial period of the reaction, if the higher reactivity of *cis*-2-butene results from the easier butyl formation, that must be ascribed to a higher probability of reaction between atomic deuterium and cis-2-butene.

In terms of the reaction kinetics above 250 K, those show high and sustained activity for the *cis-trans* isomerization, but with a similar probability with both *cis*- and *trans*-2-butenes. We do not have a completely satisfactory explanation for the loss of the *cis-trans* selectivity seen at lower temperatures, but could argue that it may involve a switch of rate-limiting step, which in this case does not depend on the nature of the hydrocarbon. The most reasonable hypothesis in our opinion is that isomerization at these high temperatures is controlled by the availability of surface deuterium atoms required for the first half-hydrogenation of the adsorbed olefin to the surface butyl intermediate. If that is the case, the reaction probability of the rate-limiting step (first half hydrogenation) would only weakly depend on the surface concentration of the molecularly adsorbed butene, and would yield similar isomerization rates for *cis*- and *trans*-2-butene despite the higher formation rates of the molecularly adsorbed *cis* isomer. In this high-temperature regime, deuterium-deficient conditions might arise from the fast desorption rate of D_2.

The other key observations from these experiments are the fact that pre-modification of the catalyst surface with carbonaceous deposits leads to a sustained and identical hydrogenation activity for both isomers but to significantly faster *cis-trans* isomerization with the *cis* isomer, since the isomerization rate with the *trans* isomer decreases by a factor of two compared to that on the initially clean surface. The nearly identical steady-state hydrogenation rates observed with both *cis* and *trans* isomers under the high-temperature conditions can be explained by a limited availability of the deuterium species absorbed in the near-surface region of the Pd particles, which were shown to be necessary for this pathway [33,34]. As a consequence, a very weak dependence of the hydrogenation rate on the surface concentration of the molecularly adsorbed olefin is expected, which results in very similar reaction rates for both *cis* and *trans* isomers even though the formation rate of surface *cis*-2-butene is expected to always be faster due to its higher thermal stability. This assumption is supported by the nearly zero-order dependence of the hydrogenation rates on the pressure of 2-butene measured at 260 K [46].

It is more difficult to understand the influence of the carbonaceous deposits on the *cis-trans* isomerization rates. What is clear is that the presence of carbon on the surface shifts the behavior back to a situation with different activities for the conversion of the *cis* and *trans* isomers. One possible reason for this may be a more pronounced destabilization of the *trans* isomer on the C-modified surface, which could lead to a considerably faster olefin desorption and hence a significantly lower total steady-state concentration of the *trans*-olefin species.

4. Conclusions

In the present report, a quantitative comparison of the catalytic activity of *cis*- vs. *trans*-2-butene with deuterium on well-defined model supported Pd/Fe_3O_4 catalyst is provided. The following key conclusions were reached from this research:

1. *cis*-2-butene is more stable than the *trans* isomer on the clean and deuterium-saturated Pd particles (66 vs. 57 kJ mol^{-1} and 47 vs. 44 kJ mol^{-1} for the clean and D-covered particles, respectively).
2. Both types of 2-butene follow similar dehydrogenation reactions, suggesting a similar decomposition mechanism.
3. In temperature-programmed desorption experiments, *cis*-2-butene yields more reaction isomerization products on the deuterium-precovered catalyst, whereas similar amounts of butane are seen with both the isomers.
4. In the isothermal molecular beam experiments, both isomers of 2-butene display high initial reactivity toward both isomerization and deuteration reactions below 215 K, but they all approach zero after prolonged olefin exposures, presumably because of the inhibition of dissociative deuterium adsorption on the surface once it becomes covered with adsorbed hydrocarbons. *cis*-2-butene exhibits higher initial rates for both reactions, but approximately the same isomerization-to-deuteration ratio as the *trans* isomer. Between 250 and 260 K, persistent *cis-trans* isomerization activity is observed, suggesting a sustained deuterium dissociation. Both *cis* and *trans* isomers show very a similar reactivity under these conditions.
5. The presence of carbonaceous species on the surface changes the catalytic behavior seen on the initially clean surface. In the high temperature regime, in particular, not only isomerization but also hydrogenation reactions can be maintained over long periods of time, the latter at similar rates with both *cis* and *trans* isomers.
6. The *cis-trans* isomerization rate with *trans*-2-butene decreases by a factor of two upon the deposition of carbon residues on the surface, whereas with *cis*-2-butene it remains as high as on the initially clean Pd particles.
7. The molecular origin of the different reactivities of *cis*- and *trans*-2-butene in the low-temperature region and the reasons for the quenching of those differences at elevated temperatures were discussed based on the qualitative kinetic analysis of the isothermal data. We refer the higher activity of *cis*-2-butene in the low-temperature (195–215 K) regime mainly to its higher stability on the surface, which results in the lower desorption rate, and hence higher formation rate of the molecularly adsorbed alkene. The disappearance of the differences in reactivity between the *cis* and *trans* isomers at elevated temperatures can be assigned to a temperature-induced change in the rate-limiting step.

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References

[1] J.M. Thomas, W.J. Thomas, Introduction to the Principles of Heterogeneous Catalysis, Academic Press, London, 1967.
[2] B.C. Gates, J.R. Katzer, G.C.A. Schuit, Chemistry of Catalytic Processes, McGraw-Hill, New York, 1979.
[3] G.C. Bond, Metal-Catalysed Reactions of Hydrocarbons, Springer Science, New York, 2005.
[4] A.P. Simopoulos in G.A. Spiller (Ed.), Handbook of Lipids in Human Nutrition, CRC Press, Boca Raton, FL, 1996, p. 91.
[5] F.E. Scarbrough, Am. J. Clin. Nutr. 65 (1997) 1578S.
[6] T.I. Taylor, in: P.H. Emmett (Ed.), Catalysis, vol. 5, Reinhold, New York, 1957, pp. 257–403.
[7] C. Kemball, in: D.D. Eley, P.W. Selwood, P.B. Weisz (Eds.), Advances in Catalysis and Related Subjects, vol. 11, Academic Press, New York, 1959, pp. 223–262.
[8] J. Horiuti, K. Miyahara, Hydrogenation of Ethylene on Metallic Catalysts; Report NSRDS-NBC No. 13, National Bureau of Standards, 1968.
[9] G.A. Somorjai, Introduction to Surface Science Chemistry and Catalysis, John Wiley and Sons, New York, 1994.
[10] F. Zaera, Prog. Surf. Sci. 69 (2001) 1.
[11] Z. Ma, F. Zaera, Surf. Sci. Rep. 61 (2006) 229.
[12] P.N. Rylander, Hydrogenation Methods, Academic Press, London, 1985.
[13] E.S. Jang, M.Y. Jung, D.B. Min, Comp. Rev. Food Sci. Food Saf. 4 (2005) 22.
[14] R.L. Burwell Jr., Acc. Chem. Res. 2 (1969) 289.
[15] I. Lee, F. Zaera, J. Am. Chem. Soc. 127 (2005) 12174.
[16] I. Lee, F. Zaera, J. Phys. Chem. B 109 (2005) 2745.
[17] I. Lee, F. Zaera, J. Phys. Chem. C 111 (2007) 10062.
[18] J.W. Veldsink, M.J. Bouma, N.-H. Schoon, A.A.C.M. Beenackers, Catal. Rev.-Sci. Eng. 39 (1997) 253.
[19] W.T. Koetsier, Lipid Technol. Appl. (1997) 265.
[20] M.W. Balakos, E.E. Hernandez, Catal. Today 35 (1997) 415.
[21] S.P. Pushpinder, J. Am. Oil Chem. Soc. 57 (1980) 850A.
[22] M.P. Gonzalez-Marcos, J.I. Gutierrez-Ortiz, C.G.-O. De Elguea, J.R. Gonzalez-Velasco, Can. J. Chem. Eng. 76 (1998) 927.
[23] F. Delbecq, F. Zaera, J. Am. Chem. Soc. 130 (2008) 14924.
[24] I. Lee, F. Delbecq, R. Morales, M.A. Albiter, F. Zaera, Nature Mater. 8 (2009) 132.
[25] I. Lee, R. Morales, M.A. Albiter, F. Zaera, Proc. Nat. Acad. Sci. 105 (2008) 15242.
[26] V.P. Zhdanov, B. Kasemo, Surf. Sci. Rep. 39 (2000) 25.
[27] C.R. Henry, Surf. Sci. Rep. 31 (1998) 231.
[28] M. Bäumer, H.-J. Freund, Prog. Surf. Sci. 61 (1999) 127.
[29] C.T. Campbell, A.W. Grant, D.E. Starr, S.C. Parker, V.A. Bondzie, Top. Catal. 14 (2001) 43.
[30] T.P.St. Clair, D.W. Goodman, Top. Catal. 13 (2000) 5.
[31] J. Libuda, I. Meusel, J. Hartmann, H.-J. Freund, Rev. Sci. Instrum. 71 (2000) 4395.
[32] B. Brandt, J.-H. Fischer, W. Ludwig, J. Libuda, F. Zaera, S. Schauermann, H.-J. Freund, J. Phys. Chem. C 112 (2008) 11408.
[33] M. Wilde, K. Fukutani, W. Ludwig, B. Brandt, J.-H. Fischer, S. Schauermann, H.-J. Freund, Angew. Chem. Int. Edition 47 (48) (2008) 9289.
[34] M. Wilde, K. Fukutani, W. Ludwig, B. Brandt, J.-H. Fischer, S. Schauermann, H.-J. Freund, Angew. Chem. 120 (48) (2008) 9430.
[35] W. Weiss, W. Ranke, Prog. Surf. Sci. 70 (2002) 1.
[36] C. Lemire, R. Meyer, V. Henrich, S.K. Shaikhutdinov, H.-J. Freund, Surf. Sci. 572 (2004) 103.
[37] T. Schalow, B. Brandt, M. Laurin, S. Schauermann, J. Libuda, H.-J. Freund, J. Catal. 242 (2006) 58.
[38] T. Schalow, B. Brandt, M. Laurin, D. Starr, Sh.K. Shaikhutdivov, J. Libuda, H.-J. Freund, Catal. Lett. 107 (2006) 189.
[39] I.C. Manzanares, V.M. Blunt, J. Peng, J. Phys. Chem. 97 (1993) 3994.
[40] D.C. McKean, M.W. Mackenzie, A.R. Morrisson, J.C. Lavalley, A. Janin, V. Fawcett, H.G.M. Edwards, Spectrochimica Acta. Part A 41A (1985) 435.
[41] N.R. Avery, N. Sheppard, Proc. R. Soc. London A 405 (1986) 27.
[42] F.M. Hoffmann, Surf. Sci. Rep. 3 (1983) 107.
[43] F. Zaera, in: J.H. Moore, N.D. Spencer (Eds.), Encyclopedia of Chemical Physics and Physical Chemistry, vol. 2, IOP Publishing Inc., Philadelphia, 2001, pp. 1563–1581.
[44] H. Öfner, H. Zaera, F.J. Phys. Chem. 101 (1997) 396.
[45] P.A. Redhead, Vacuum 12 (1962) 203.
[46] To be published.
[47] A.M. Doyle, Sh.K. Shaikhutdinov, H.-J. Freund, J. Catal. 223 (2004) 444.
[48] X.-C. Guo, R.J. Madix, J. Catal. 155 (1995) 336.

[49] M.A. Chesters, C. De La Cruz, P. Gardner, E.M. McCash, P. Pudney, G. Shahid, N. Sheppard, J. Chem. Soc. Faraday Trans. 86 (1990) 2757.
[50] J.C. Bertolini, A. Cassuto, Y. Jugnet, J. Massardier, B. Tardy, G. Tourillon, Surf. Sci. 349 (1996) 88.
[51] G. Tourillon, A. Cassuto, Y. Jugnet, J. Massardier, J.C. Bertolini, J. Chem. Soc. Faraday Trans. 92 (1996) 4835.
[52] M.A. Chesters, A.B. Horn, L.M. Ilharco, A.I. Ransley, B.H. Sakakini, J.C. Veckerman, Surf. Sci. 251/252 (1991) 291.
[53] N.R. Avery, N. Sheppard, Surf. Sci. Lett. 169 (1986) L367.
[54] J. Horiuti, M. Polanyi, Trans. Faraday. Soc. 30 (1934) 1164.
[55] F. Zaera, Chem. Rev. 95 (1995) 2651.
[56] F. Zaera, Acc. Chem. Res. 25 (1992) 260.