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Olefin hydrogenation on Pd model supported catalysts: New mechanistic insights

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ABSTRACT

Hydrogenation of unsaturated hydrocarbon compounds, catalyzed by transition metals, is traditionally believed to be a structure-insensitive reaction. Recent progress in understanding the microscopic details of hydrogenation processes now challenges the universality of this common belief. In this perspective article, we present results on the hydrogenation of *cis*-2-butene: over Pd model nanoparticles supported on an Fe_3O_4/Pt(111) oxide thin film and over a Pd(111) single crystal. We provide direct experimental evidence that the hydrogenation activity of Pd is strongly dependent on the presence of hydrogen species absorbed in the subsurface region of the metal catalyst and is governed by the permeability of the surface for hydrogen. Since the formation of subsurface hydrogen species in Pd is a strongly structure-sensitive process, the low-coordinated surface sites, such as edges and corners on Pd nanoclusters, play a crucial role in replenishment of the subsurface hydrogen reservoir and maintaining the hydrogenation activity under steady-state conditions. We show that selective modification of these low-coordinated surface sites on Pd nanoclusters with carbon allows for faster subsurface hydrogen diffusion and thereby results in sustained hydrogenation activity, a result that cannot be achieved on C-free Pd nanoparticles, nor on C-free Pd(111), nor on C-containing Pd(111). Theoretical calculations support the proposed facilitation of subsurface hydrogen diffusion through C-modified low-coordinated surface sites on Pd nanoclusters and show the conceptual importance of atomic flexibility of nanoparticles in hydrogenation catalysis.

1. Introduction: toward an understanding of heterogeneously catalyzed hydrogenation at the microscopic level

Heterogeneously catalyzed hydrogenation on metals is responsible for the formation and interconversion of some of the most basic molecules and has long been of industrial and academic interest [1,2]. Partial and full hydrogenation of unsaturated hydrocarbons, in particular, is of immense importance since it provides large-scale manufacturing of both valuable intermediates for many chemical processes and commodity chemicals. This type of reactions was extensively investigated in early years using conventional catalytic techniques [1,3] and more recently by modern surface science methodologies [2,4,5].

Despite numerous efforts to study the catalyzed hydrogenation, there is still only little fundamental understanding of the mechanistic details and kinetics of the underlying surface processes occurring on realistic nanostructured catalysts. The main reason for the lack of atomistic insights into surface hydrogenation reactions is the poor transferability of the results from model surface science studies to realistic hydrogenation processes. While under realistic reaction conditions, hydrogenation typically occurs on complex multi-component nanostructured metal-oxide systems that can be further modified by deposits resulting from early decomposition of hydrocarbons [1], the majority of surface science studies focus on simple single-crystal surfaces in clean ultra-high-vacuum conditions. In many cases, such simplified model surfaces fail to adequately reproduce the full spectrum of structural properties inherent to realistic catalysts, such as particle size or support effects, which can be crucial for determining the overall catalytic activity and selectivity.

It is obvious that a truly fundamental understanding of catalytic activity and selectivity would require a direct experimental link between the microscopic structure of metal-oxide catalysts and the role of particular structural features in reaction mechanisms and kinetics. As a strategy to approach this goal, model nanostructured catalysts have recently been developed [6–9]. Such surfaces allow us to introduce certain structural features in a well-controlled manner, while still remaining easily accessible to the full spectrum of experimental methods available in surface science, to obtain a comprehensive microscopic picture of the catalyst's surface. A large variety of model systems were developed and extensively characterized, employing both thin oxide films and oxides as support [6–9].

There is a broad range of practically important aspects of hydrogenation catalysis that need to be addressed in the atomistic-level studies. For example, it has been recognized in the catalytic community for a long time that accumulation of carbonaceous deposits

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(resulting from early decomposition of hydrocarbon reactants) considerably affects the activity and especially the selectivity for hydrocarbon conversions with hydrogen on transition metals [12,10]. The underlying microscopic mechanisms of the carbon-induced changes in the reactivity remained unclear until recently. There is also an ongoing discussion about possible involvement of subsurface hydrogen species (absorbed below the outermost surface layer or in the volume of metal nanoparticles) in olefin hydrogenation [11–13]. The traditional opinion that only surface hydrogen species participate in the hydrogenation process was questioned for the first time by Ceyer and coworkers studying ethylene hydrogenation on Ni(1 1 1) [11]. More recently, other experimental and theoretical evidences for the important role of subsurface hydrogen were reported [12,13]. However, this potential involvement of subsurface hydrogen in the hydrogenation of the double bond remained a controversial issue for a long time [14], mainly because of the lack of experimental techniques capable of separately monitoring different hydrogen species under the reaction conditions. This scenario can potentially result in some important implications for the overall activity and selectivity of the hydrogenation catalyst: if one of the key reaction participants – subsurface hydrogen – can be only slowly replenished under reaction conditions, the hydrogen permeability of the metal surface can play a crucial role in the reaction kinetics. Since subsurface hydrogen diffusion [15] is known to be a highly structure-sensitive process [16–19] – particularly on Pd, which is commonly used for hydrogenation – the specific structure of the metal nanoclusters and the degree of coordination of the surface metal atoms can be important in determining the formation and replenishment rate of subsurface hydrogen and therefore may be decisive for hydrogenation activity.

These recent findings and hypotheses clearly demonstrate the need for more precise nanostructured catalytic systems as models for hydrocarbon conversions with hydrogen. In particular, studies on small metal nanoparticles supported on model planar oxide substrates under well-controlled conditions were envisaged to provide fundamental insights into the mechanisms of olefin hydrogenation at the atomic scale [6,12], and elucidate the role of surface modifiers.

In this perspective article, we summarize key results from our studies on the mechanism and kinetics of olefin conversions with hydrogen over well-defined nanostructured model supported catalysts [20–27]. Our approach involves the application of molecular beam techniques and infrared reflection–absorption spectroscopy to obtain detailed insights into atomistic details of olefin hydrogenation and isomerization. As model catalysts, we utilize Pd nanoparticles supported on a well-ordered Fe_3O_4 thin film grown on a Pt(1 1 1) single crystal [28]. The same types of reactions were also investigated on Pd single-crystal surfaces to identify which reactivity features can be traced back to the structural properties specific to Pd nanoparticles. Complementary nuclear reaction analysis (NRA) experiments for hydrogen depth profiling [21,29] and theoretical calculations [23] provided important information on the details of hydrogen interaction with Pd.

Three main results were obtained in the present studies: (i) hydrogenation of the olefinic double bond was shown to require the presence of subsurface hydrogen and a particular reaction step – the second half-hydrogenation – was identified as linked to the availability of subsurface hydrogen species; (ii) it was observed that sustained hydrogenation can be achieved only on the Pd nanoparticles, and only when the low-coordinated surface sites (edges and corners) were modified by adsorbed carbon. Neither C-free Pd nanoparticles nor C-free or C-modified Pd(1 1 1) surface was found to be capable of maintaining hydrogenation activity under steady-state conditions; (iii) this unique role of carbonaceous deposits was explained by a pronounced facilitation of diffusion of hydrogen into the subsurface of Pd nanoparticles through C-modified low-coordinated surface sites, thereby allowing fast replenishment of the reservoir of active subsurface hydrogen species under steady-state reaction conditions. Both theoretical and experimental evidence was found for facilitated hydrogen penetration into the volume of Pd nanoclusters due to the C-modification of low-coordinated surface sites.

2. Selectivity toward *cis–trans* isomerization and hydrogenation of olefins on clean and C-modified Pd nanoparticles

One of the important questions that was addressed in our studies is how does the activity and selectivity of competing reaction pathways of olefin conversions with hydrogen depend on the structure of the metal nanoclusters and on the presence of surface modifiers such as strongly dehydrogenated carbonaceous species that are typically formed on transition metals during the early stages of reaction? Generally, olefin conversions with H_2 are accounted for by the Horiuti–Polanyi mechanism, which proceeds through a series of successive hydrogenation–dehydrogenation steps [30]. Specifically for *cis*-2-butene, investigated in this study, a first half-hydrogenation step forms a surface butyl species, which is a common reaction intermediate for both the *cis–trans* isomerization pathway (this pathway is also accompanied by an H-D exchange if the reaction is carried out with deuterium) and the hydrogenation (deuteration) pathway [31]. This butyl intermediate can either undergo a β-hydride elimination to form *trans*-2-butene-d_1, or can incorporate a second D atom to form butane-d_2 via the second half-hydrogenation step. Dehydrogenation of the adsorbed alkene to other carbonaceous surface species is also

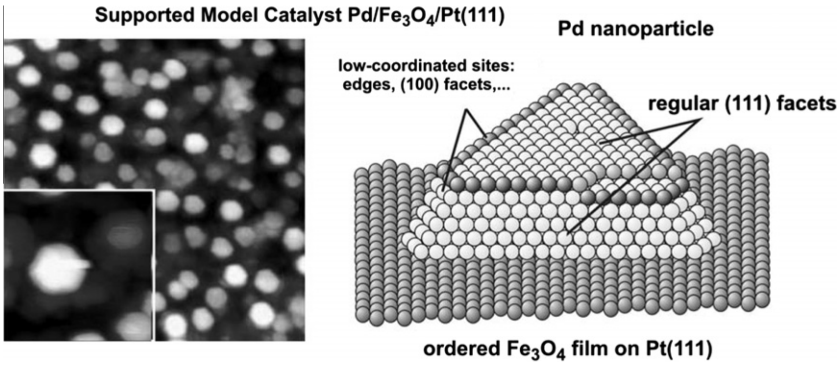
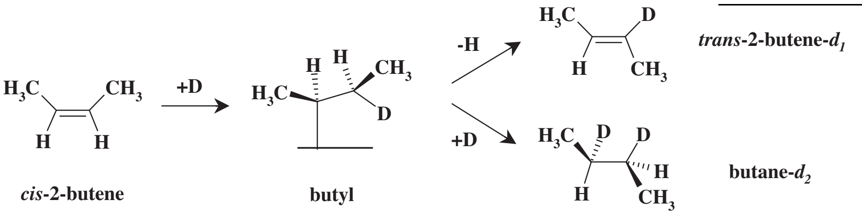


Fig. 1. Scanning tunneling microscopy (STM) image (100 nm × 100 nm, inset: 20 nm × 20 nm) of the Pd/Fe_3O_4/Pt(1 1 1) supported model catalyst [28] used in the experiments described here, together with a schematic representation of the structure of the supported Pd nanoparticles.

possible, giving rise to the accumulation of different partially (or fully) dehydrogenated hydrocarbon species [2,4].



The formation rates of the two primary reaction products – *trans*-2-butene-d_1 and butane-d_2 – were probed under isothermal conditions. Two independent molecular beams were used to dose the reactants – *cis*-2-butene and $D_{2,}$ – with the evolution of gas-phase products monitored as a function of time by quadrupole mass spectrometry. As a model catalyst, Pd nanoparticles supported on thin planar Fe_3O_4 film were used, shown in Fig. 1. This well-defined surface was prepared *in situ* under ultra-high-vacuum conditions on a planar Pt(1 1 1) substrate [28]. The Pd nanoclusters are on average 6 nm in diameter and exhibit mainly (1 1 1) facets (~80%) and a smaller fraction of (1 0 0) facets and other low-coordinated surface sites such as edges and corners (~20%). It has been spectroscopically shown in our previous studies [20,32] that when sub-monolayer amount of C is produced on the Pd nanoclusters, it selectively blocks the low-coordinated surface sites while leaving the majority of the regular (1 1 1) facets C-free. We used both types of catalyst – C-free and C-modified (with the edges and corners covered by C) – to compare their catalytic activities and selectivities with regard to the competing hydrogenation and *cis–trans* isomerization pathways. C was produced by thermal decomposition of the olefin [20], and the spatial distribution of the resulting carbonaceous deposits was characterized by IRAS using CO molecule as a probe for different adsorption sites [20,24].

Fig. 2 displays the results of reaction rate measurements for hydrogenation and *cis–trans* isomerization of *cis*-2-butene on the initially clean (Fig. 2a) and C-modified (Fig. 2b and c) Pd nanoparticles [20,21]. The catalyst was first pre-exposed to a continuous D_2 beam to saturate the particles, and then a sequence of *cis*-2-butene pulses was applied using an independent beam source along with continuous D_2 exposure. The reaction was carried out in a large excess of gas-phase D_2 exposure with a flux ratio of D_2/*cis*-2-butene = 760. On the initially clean particles (Fig. 2a), both reaction pathways exhibit a short induction period, in which various strongly adsorbed surface species are formed [20], followed by a transient period of high activity. However, for C-free particles at 260 K, only *cis–trans* isomerization activity is sustained over extended periods of time, whereas the hydrogenation rate quickly decreases and returns to zero. Remarkably, not only isomerization but also hydrogenation is maintained under steady-state conditions on the catalyst that was C-modified prior to reaction (Fig. 2b). This unique catalytic behavior clearly demonstrates the promoting role of C in the persistent hydrogenation activity of the Pd catalyst [21,25].

Detailed kinetic analysis of both reaction rates strongly suggests that two non-equivalent D species must be involved in the first and the second half-hydrogenation steps to produce butane-d_2. Indeed, the sustained *cis–trans* isomerization rate evidences the fast formation of the common butyl-d_1 reaction intermediate and with this suggests sufficient availability of both the adsorbed *cis*-2-butene species and the surface D atoms. However, the availability of these D atoms, which are involved in the first half-hydrogenation step, is apparently not a sufficient condition for the second half-hydrogenation to butane-d_2. Rather, the presence of a special type of D atom must be required for the second half-hydrogenation step, which will be further indicated as D^*. These D^* species are obviously present on the Pd particles pre-saturated with deuterium as at the beginning of the olefin exposure they give rise to a high hydrogenation rate. However, they cannot be replenished under steady-state conditions on clean Pd particles, resulting in selective suppression of hydrogenation. The conclusion of the involvement of two non-equivalent D

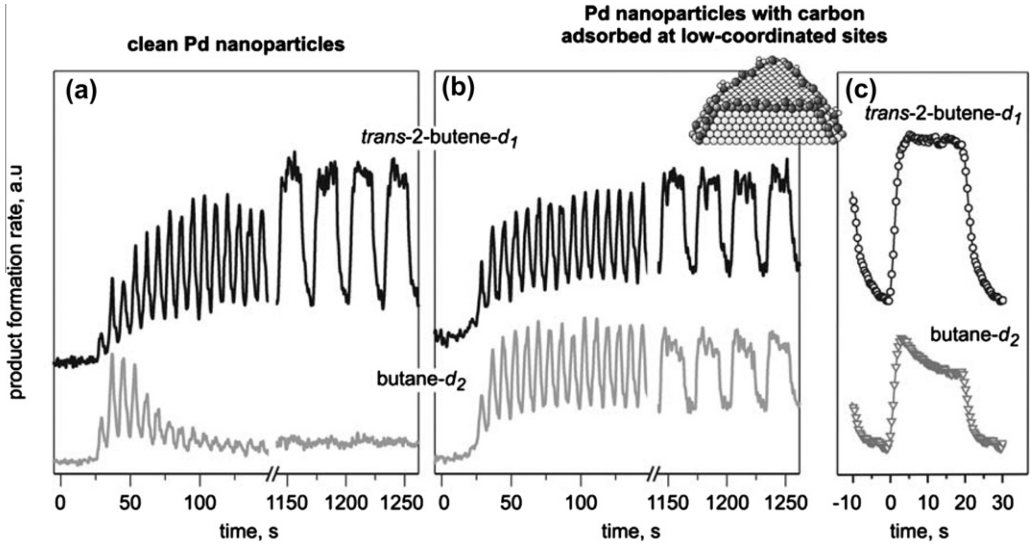


Fig. 2. Results from isothermal pulsed molecular beam experiments on the conversion of *cis*-2-butene with D_2 at 260 K on (a) initially clean and (b) C-modified Pd/Fe_3O_4/Pt(1 1 1) model catalysts. Shown is the evolution of the reaction rates as a function of time for *trans*-2-butene-d_1 (black curves) and butane-d_2 (gray curves). The catalysts were exposed to D_2 beam continuously, the *cis*-2-butene beam was pulsed; (c) average reaction rates calculated for *cis–trans* isomerization (black curve) and hydrogenation (gray curve) from the last 30 long pulses of the dataset show in (b).

atoms in the two individual hydrogenation steps is also in agreement with the kinetic analysis of the pulse profiles obtained for products under steady-state conditions (Fig. 2c) [24,26]. Here, the averaged reaction rates are shown, obtained upon the modulation of the olefin beam under steady-state conditions with C-modified Pd particles. Prior to each pulse, the surface was exposed to the continuous D_2 beam in order to re-saturate the particles with D species, so that the reactivity immediately after resuming the *cis*-2-butene beam corresponds to the reactivity of the catalyst when it is saturated with D. For *cis–trans* isomerization (upper trace) and hydrogenation (lower trace), two different pulse profiles were observed. While the isomerization rate reaches its steady-state value nearly instantaneously and then remains constant during the duration of pulse, the hydrogenation rate shows the highest reactivity at the beginning of the pulse but then decreases to a significantly lower value upon continuing olefin exposure. The former type of response is indicative of reaction conditions under which the surface concentrations of the reactants (*cis*-2-butene and surface D) and of the reaction intermediate (butyl-d_1) remain constant during the olefin pulse [26]. The decreasing hydrogenation rate shows a behavior that is typical for a reaction regime in which the availability of one of the reactants is high at the beginning of the olefin exposure, but decreases as the reaction proceeds [26]. In view of the fact that the surface concentration of the butyl-d_1 species remains constant (as indicated by the constant *cis–trans* isomerization rate), the decreasing hydrogenation rate seen toward the end of the pulse must be due to the depletion of the second species, D^*, that is required for second half-hydrogenation of butyl-d_1. Indeed, the concentration of this D^* species must decrease over duration of the pulse without affecting the *cis–trans* isomerization rate (i.e., the surface concentrations of butyl-d_1 and D), while still leading to selective decrease in hydrogenation rate only. In agreement with the discussion above, the clearly different pulse profiles observed can be explained only by assuming that non-equivalent D species participate in the first and second half-hydrogenation steps of *cis*-2-butene.

In the following, we will address two closely related questions: what is the nature of this special type of D^* species and how does C promote the sustained hydrogenation activity?

3. Involvement of subsurface hydrogen in olefin hydrogenation. Role of carbon modification in inducing sustained hydrogenation

As a next step, we identified the nature of the specific D^* species involved in the second half-hydrogenation of the olefinic bond. Our experimental approach combined measurement of the concentrations of surface and subsurface H species by NRA for hydrogen depth profiling [21,29], complemented by transient molecular beam experiments to measure the reaction rates [21]. The former method (described in detail in [29]) was used to independently monitor the concentrations of the surface-adsorbed and subsurface (or volume-absorbed) H species as a function of hydrogen pressure in the environment. Briefly, a highly pronounced pressure dependence was observed for the concentration of subsurface H species in the H_2 pressure region relevant for this study (10^{-7}–2×10^{-5} mbar). In contrast, the saturation coverage of surface H species was found to be reached already below 10^{-6} mbar and this coverage could not be further increased by applying higher H_2 pressures. These findings are in agreement with the results of other previous experimental and theoretical studies which indicate that H binds much stronger on the surface (~0.8 eV per Pd atom) than in the subsurface (~0.4 eV). [33] Additionally, H dissociation on the surface is known to be a non-activated process, whereas the formation of subsurface hydrogen proceeds through an activated step of H penetration below the surface layer (indicated further as subsurface hydrogen diffusion) [16,34]. These results indicate that the strongly binding surface adsorption state populates first and the population of the subsurface hydrogen depends more strongly on the H_2 pressure in the environment. These experimental observations were complemented by the reactivity measurements in pulsed molecular beam experiments, where the reaction rates of the competing *cis–trans* isomerization and hydrogenation pathways were investigated as a function of the D_2 pressure.

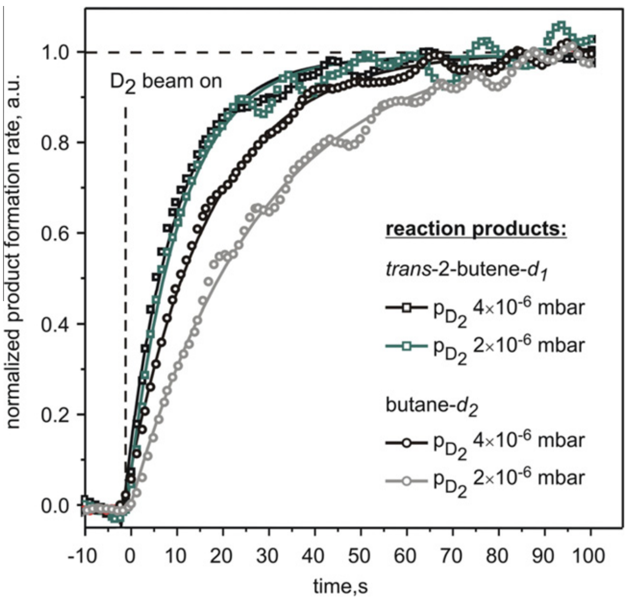


Fig. 3. Time evolution of the normalized reaction rates for the *cis–trans* isomerization (*trans*-2-butene-d_1) and hydrogenation (butane-d_2) products in the *cis*-2-butene + D_2 reaction after a temporary intermission of the D_2 beam. The reaction rates are obtained at 260 K over the C-modified Pd/Fe_3O_4/Pt(1 1 1) catalyst at different D_2 pressures (2×10^{-6} and 4×10^{-6} mbar) with the ratio *cis*-2-butene:D_2 kept constant.

The results of relaxation-kinetics molecular beam experiments on the C-modified Pd/Fe_3O_4/Pt(1 1 1) catalyst are displayed in Fig. 3 [21]. The model catalyst was pre-exposed to D_2 and *cis*-2-butene to reach the steady-state regime, and then the D_2 beam was switched off for 100 s until the D reservoir on/in the Pd particles was depleted as indicated by vanishing reaction rates. Thereafter, the D_2 beam was switched on again and the evolution of isomerization (*trans*-2-butene-d_1) and hydrogenation (butane-d_2) products was monitored as a function of time. The main idea of this experiment was to re-populate different D species – surface and subsurface ones – with different time constants and to monitor how fast the reaction rates of both competing reaction pathways return to their steady-state value as in response to this perturbation. It should be emphasized that the time evolution of both reaction products will be limited by the formation rate of the atomic D species on and/or in the Pd clusters, which are covered with hydrocarbons. Based on the above discussion of D(H) binding strength in the different states, it can be expected that steady-state concentration of surface D will be reached first and the concentration of subsurface D will recover with some delay. Moreover, the aforementioned strong dependence of the subsurface D(H) concentration on the D_2(H_2) pressure also suggests that the characteristic time for replenishing the subsurface reservoir should be strongly dependent on the D_2(H_2) pressure.

The modulation experiments were carried out for two different D_2 pressures (4×10^{-6} and 2×10^{-6} mbar) with a constant *cis*-2-butene:D_2 ratio of 2×10^{-3}. In both cases, all reaction rates returned to exactly the same steady-state levels regime after the D_2 beam is turned on again. However, the transient time evolution for the reaction products of the two pathways exhibits very different behaviors and D_2 pressure dependences. At both D_2 pressures, the isomerization rate was observed to return to the steady-state level with short and nearly identical time constants: $\tau = 11.0 \pm 0.3$ and 11.4 ± 0.3 s. In contrast, the evolution of the hydrogenation rate during relaxation is substantially slower and exhibits a pronounced pressure dependence with characteristic times of 18.3 ± 0.3 s and 28.3 ± 0.5 s for 4×10^{-6} and 2×10^{-6} mbar of D_2, respectively.

The fast and pressure-independent time evolution of the isomerization product suggests that this pathway is linked to the coverage of surface D atoms. The pronounced pressure dependence of the hydrogenation rate, on the other hand, identifies the D species involved in the second half-hydrogenation step as strongly sensitive to the D_2 pressure. In combination with the NRA results [21], this observation strongly suggests that subsurface H(D) species are required for the second step in hydrogenation. It is also important to note that the D species, which is required for hydrogenation, cannot be the surface-adsorbed D, as in that case the time evolution of the hydrogenation product, butane-d_2, would display a pressure independence like that of the isomerization product, *trans*-2-butene-d_1. The substantially slower recovery of the hydrogenation rate as compared to the isomerization rate is a natural consequence of the fact that for subsurface site population the D atoms have to diffuse from the surface into the cluster volume, which is an activated process, whereas D_2 dissociation on the Pd surface is non-activated [16].

There are two feasible explanations for the involvement of subsurface H species in the second half-hydrogenation step. First, the reaction between subsurface H and the butyl intermediate can have lower activation barrier than recombination of surface H species with butyl. Theoretical calculations by Ledentu et al. and Michaelides et al. [35] confirm this hypothesis. Alternatively, subsurface hydrogen can merely modify the electronic and/or adsorption properties of surface H species (e.g., by lowering the binding energy) and with this make it more active for attacking the metal–carbon bond. In this case, the subsurface H species is not directly involved in the second half-hydrogenation step but acts indirectly as a modifier of adsorption properties of surface H. Further theoretical work is needed to understand the underlying microscopic mechanism of this process. It should be also noted that the influence of subsurface hydrogen cannot be explained by strong weakening the butyl-Pd bond since in this case the competing reaction pathway – *cis–trans* isomerization proceeding through the same reaction intermediate – would be also strongly affected by the presence or absence of subsurface H, which was not observed experimentally.

Having established the nature of the H(D) atoms involved in hydrogenation, which is in agreement with theoretical predictions [35], we can now explain the observations displayed in Fig. 2. On the initially clean particles pre-saturated with D_2 prior to olefin exposure, both surface and subsurface hydrogen are populated, which results in the high initial rates of both reaction pathways. After the prolonged olefin exposure, hydrogenation becomes selectively suppressed because the subsurface D^* species are depleted and cannot be replenished under the steady-state reaction conditions. Apparently, the inability to populate subsurface D arises from hindered D subsurface diffusion under the steady-state reaction conditions with the surface covered with hydrocarbons.

The sustained hydrogenation activity observed on the C-modified catalyst suggests that the C-modified surface is capable of more rapidly replenishing subsurface D under steady-state conditions. This means that the co-adsorbed carbonaceous species most likely facilitate D diffusion from the surface into the particle volume.

4. Hydrogenation on C-free and C-modified Pd nanoparticles and the Pd(1 1 1) single-crystal surface: role of low-coordinated surface sites and their modification by carbon

In the above presented study, we obtained direct experimental evidence for the involvement of subsurface hydrogen in the second half-hydrogenation step [21]. Additionally, slow replenishment of the subsurface H species was identified as the rate-determining step in olefin hydrogenation in a broad range of reaction conditions [26]. In view of these results, the permeability of the metal surface for hydrogen can play a crucial role for its activity in hydrogenation catalysis. Since subsurface hydrogen diffusion is known to be a strongly structure-sensitive process on Pd surfaces [16,18,19], the particular structure of the nanocluster and the degree of coordination of the surface Pd atoms can be important in determining the formation rate of subsurface hydrogen species and therefore may be decisive for the hydrogenation activity. In line with this hypothesis, it was observed that modification of the low-coordinated surface sites of Pd nanoparticles, such as edges and corners, with C significantly affects the hydrogenation activity and results in a sustained hydrogenation rate that is not possible on the C-free surface (see Fig. 2) [20,21].

In order to obtain more insights into the role of low-coordinated surface sites in hydrogenation, two complementary experimental strategies were applied: first, we compare the hydrogenation activity on Pd nanoparticles with that on an extended Pd(1 1 1) single-crystal surface. Secondly, we selectively modify the low-coordinated surface sites by deposition of C, which was previously determined to predominantly occupy edges and corners of Pd nanoclusters, and follow the reactivity changes upon such modification [25].

The experiments were carried out in the same way as described in Section 2. Fig. 4 shows the evolution of the hydrogenation rate in the transient regime, when the reaction starts from a D-saturated surface (Fig. 4a), and the hydrogenation rate under steady-state conditions (Fig. 4b and c) on clean and C-modified Pd nanoparticles (upper row) and the corresponding Pd(1 1 1) single crystals (lower row). The measured hydrogenation rates were normalized to the number of the surface Pd atoms for comparison (1.5×10^{15} Pd atoms·cm^{-2} for Pd(1 1 1) and 0.6×10^{15} Pd atoms cm^{-2} for Pd nanoparticles.

The initial hydrogenation rates on Pd(1 1 1) and Pd nanoparticles, both pre-saturated with D_2, were found to be of the same order of magnitude (Fig. 4a). This observation clearly demonstrates that under conditions where there are no limitations in D availability (for both surface and subsurface species), the intrinsic activity of Pd nanoparticles – comprising both (1 1 1) facets and low-coordinated surface sites – is very similar to that of Pd(1 1 1). However, under steady-state conditions, the overall reactivity of investigated surfaces differs. Thus, on both C-free surfaces, no sustained hydrogenation can be observed, which points to limitations in availability of subsurface D species. As was discussed previously, C deposition changes the steady-state hydrogenation rate on Pd nanoparticles dramatically: a sustained hydrogenation rate is observed, with a value that is nearly identical to the initial hydrogenation rate on the D-saturated particles (see also Fig. 2a) [21,20,25]. This effect cannot be obtained on C-modified Pd(1 1 1), where the hydrogenation rate in steady state remains negligible even after C deposition. It should be emphasized that on all four catalysts (C-free and C-modified Pd(1 1 1) and Pd particles), the rate of the competing reaction pathway (*cis–trans* isomerization/H-D exchange) was observed to be in the same range. This fact strongly suggests that the pronounced steady-state hydrogenation rate on the C-modified Pd particles, which is by several orders of magnitude higher than on C-modified Pd(1 1 1), cannot be ascribed to

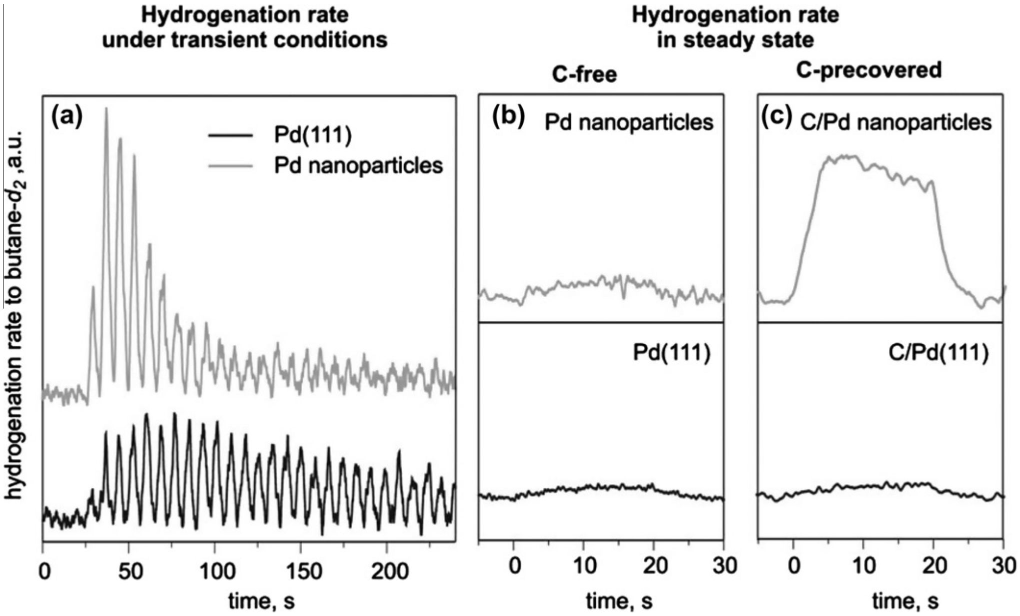


Fig. 4. Comparison on the hydrogenation rates of *cis*-2-butene over Pd nanoparticles (gray curves) and Pd(1 1 1) (black curves). The hydrogenation rates are normalized to the number of the surface Pd atoms. Shown are (a) the initial hydrogenation rates on C-free surfaces pre-saturated with D_2; (b and c) averaged hydrogenation rates obtained under the steady-state conditions, at which limitations in availability of subsurface D can occur. On both C-free surfaces (b) no sustained hydrogenation was observed, while C deposition induces persistent hydrogenation activity on Pd nanoclusters but not on Pd(1 1 1) (c).

strong variations in the concentrations of *cis*-2-butene and *surface* D. This behavior implies that sustained hydrogenation on C-modified Pd nanoparticles arises from the modified properties of the low-coordinated surface sites and *not* from a C-induced modification of regular (1 1 1) terraces.

There is only one conceivable way to rationalize the role of low-coordinated surface sites in promotion of the long-time sustained hydrogenation activity on C-modified Pd nanoparticles. The persistent hydrogenation can be explained only by a more effective replenishment of the reactive species under steady-state reaction conditions compared with the C-free surface. Since for all four catalysts (C-modified and C-free Pd nanoparticles and Pd(1 1 1)), the *surface* D species and adsorbed *cis*-2-butene appear to be present in comparable amounts based on the steady-state *cis–trans* isomerization/H-D exchange rates, the only reactant remaining, for which the abundance can be significantly affected by C, is *subsurface* D. At a microscopic level, this scenario implies that C deposition at low-coordinated sites on Pd nanoparticles renders the catalyst to be highly permeable for D and consequently enables the system to maintain a *subsurface* D concentration at or sufficiently close to the initially high level. This would result in the persistent hydrogenation activity observed, which is maintained at the same level as with the initial reactivity for D pre-saturated particles (see Fig. 2b and Fig. 4a and c). It should also be emphasized that C-modification of particle edges does not result in hydrogenation rates higher than on the D-saturated surface at the beginning of the experiment, which means that the modified surface sites are *not* inherently more active in hydrogenation. Instead, C-modification merely allows the maintaining of high populations of reactants, particularly *subsurface* D at a sufficiently high level [20,21,24,25].

These results provide straightforward experimental evidence that low-coordinated surface sites can play a crucial role in hydrogenation processes. The microscopic mechanism of their action is most likely based on determining how fast H(D) can penetrate into the subsurface region of Pd nanoparticles in order to produce the subsurface H(D) species required for hydrogenation. On particles with C-modified low-coordinated sites, subsurface H(D) diffusion appears to be much faster than on the C-free particles, which results in fast replenishing of the subsurface reservoir and in steady-state hydrogenation rates similar to the initial hydrogenation rates observed on the D-saturated surface.

Recent theoretical calculation supported this hypothesis and showed that a pronounced expansion of the Pd lattice near the particle edges can be achieved by the modification of the low-coordinated sites with adsorbed C, which nearly lifts the activation barrier for hydrogen subsurface diffusion [23]. In contrast, the lateral rigidity of the extended Pd(1 1 1) surface was demonstrated to hinder lattice expansion, and therefore, almost no effect on the activation barrier for hydrogen subsurface diffusion was observed on extended Pd(1 1 1) surface. These theoretical predictions are in an excellent agreement with the experimental observations, showing that C deposition allows maintaining the hydrogenation rate on atomically flexible Pd nanoclusters but has no effect for laterally rigid Pd(1 1 1) surface [25]. These computational results demonstrated the conceptual importance of the atomic flexibility of sites near particle edges that, in contrast to intrinsically rigid regular single-crystal surfaces, plays a crucial role in H subsurface diffusion on Pd.

5. The rate of subsurface hydrogen diffusion on clean and C-modified Pd nanoparticles and Pd(1 1 1): HD exchange experiments

As a final step, we sought to provide a direct experimental proof for faster subsurface hydrogen diffusion due to C-modified low-coordinated surface sites on Pd nanoparticles. Particular emphasis was placed on understanding the role of atomically flexible low-coordinated surface sites, such as edges and corners that are present on the nanoparticles, on the diffusion process, and on exploring how modification of these surface sites with C affects the subsurface diffusion rate. To probe hydrogen subsurface diffusion, the $H_2 + D_2 \rightarrow HD$ exchange reaction was conducted in the temperature regime where this reaction is limited by the formation rate of subsurface H(D) species. The full details of these experiments can be found elsewhere [27]. Briefly, it was previously shown by

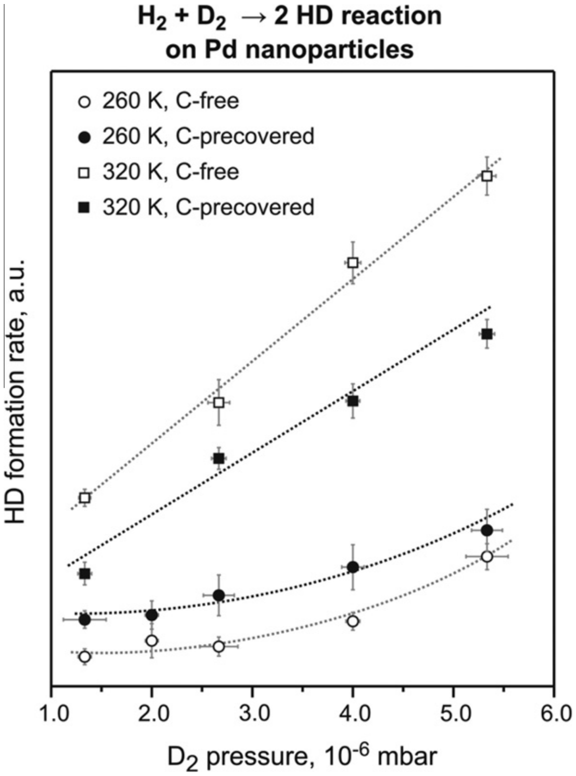


Fig. 5. The steady-state HD formation rates obtained on the pristine and C-precovered Pd nanoparticles supported on Fe_3O_4/Pt(1 1 1) at 260 and 320 K in the D_2 pressure range from 1.3×10^{-6} to 5.3×10^{-6} mbar. The reactant ratio D_2:H_2 was kept constant at 71. C deposition result in the ~30% decrease in the HD formation rate at 320 K and in ~100% increase in the reaction rate at 260 K.

combination of TPD and NRA experiments [29] that formation of HD can occur either via recombination of two surface H and D species or it can involve subsurface H or D species. The former pathway proceeds only at temperatures above 300 K [16,29,36], while the latter pathway dominates at lower temperature (between 200 and 300 K) [29]. The exact mechanism of how subsurface H(D) species are involved in HD formation is not clear. Our experimental results are consistent with the scenario implying that one subsurface atom recombines with a surface atom to form HD. In the case of slow subsurface hydrogen diffusion, the formation rate of subsurface species will be the limiting step in HD production and therefore can be addressed by probing the rate of isotopic scrambling. For full details, the reader is referred to the original publication [27].

Fig. 5 shows the steady-state HD formation rates obtained during D_2 and H_2 exposure for the reaction temperatures 260 and 320 K on clean and C-modified Pd nanoparticles for a range of pressure conditions with a constant D_2:H_2 ratio. C modification was found to affect the HD formation rate in a dramatically different way for the two reaction temperatures: whereas at 320 K preadsorbed C *reduces* the overall reaction rate by about 30%, the reaction rate *increases* by about 100% at 260 K on the C-modified particles for all pressures studied. The decreased HD formation rate in the high-temperature regime, where HD formation is dominated by the recombination of the surface H and D species, can be easily rationalized as a consequence of the blocking of surface adsorption sites by C. Interestingly, even though a part of the surface is blocked by C, the HD formation rate is significantly increased in the low-temperature regime, where desorption involves at least one subsurface H(D) species. This effect can be explained only by the higher formation rate of the subsurface H(D) species on the C-modified particles resulting in a higher steady-state concentration of the species in the subsurface [27]. It should be noted that at the microscopic level, facilitation of the subsurface H diffusion through the C-modified low-coordinated sites is most likely even more pronounced. Indeed, the nearly 100% increase in the overall subsurface diffusion rate arises from modification of only the ~20% of the surface sites constituting edges and corners of Pd particles. Microscopically, this means that the *local* diffusion rate through these C-modified sites increases by at least an order of magnitude. These results are in the excellent qualitative and in good quantitative agreement with the theoretical predictions [23].

With this and other experimental observations [27], we provide direct experimental evidence that – inline with the theoretical predictions – the atomically flexible low-coordinated surface sites on Pd particles play a crucial role in the diffusion process and that their selective modification with C results in marked facilitation of subsurface hydrogen diffusion. The latter finding allows us to identify adsorbed C as an exceptionally important participant in surface reactions, which governs the rate of subsurface hydrogen diffusion, and to revisit the traditional view of the role of carbonaceous deposits in hydrogenation chemistry.

6. Conclusions and future trends

Summarizing, by performing molecular beam experiments on olefin conversions with hydrogen over well-defined Pd nanoparticles supported on Fe_3O_4/Pt(1 1 1) oxide films and Pd(1 1 1), we

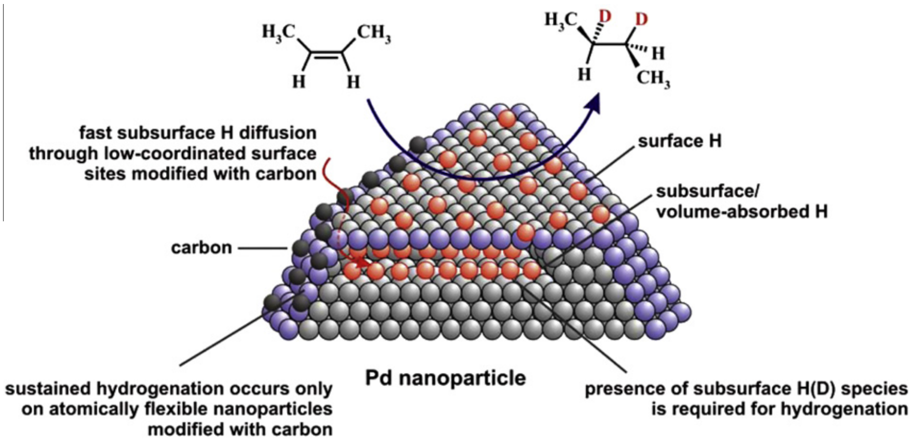


Fig. 6. Proposed reaction mechanism of olefin hydrogenation on Pd nanoparticles.

obtained a comprehensive microscopic picture of hydrogenation and isomerization processes on the nanostructured catalysts (see model in Fig. 6). First, by combination with the results of NRA for hydrogen depth profiling, we obtained direct experimental evidence that the presence of subsurface hydrogen is required for hydrogenation pathway and this hydrogen species is involved – directly or indirectly – in the second half-hydrogenation of the alkyl intermediate. *cis*–*trans* isomerization of *cis*-2-butene was observed to be sustained on all investigated surfaces and the presence of only surface H(D) species was concluded to be sufficient for this reaction pathway. In contrast, the hydrogenation pathway could be maintained only on Pd nanoparticles, at which the low-coordinated surface sites such as edges and corners were modified by the deposition of strongly dehydrogenated carbonaceous deposits. Neither C-free Pd particles nor C-free and C-modified Pd(1 1 1) surfaces were found to be able of maintaining the hydrogenation rate under the steady-state reaction conditions. We ascribe this promoting effect of C on Pd nanoparticles to pronounced facilitation of subsurface hydrogen diffusion into the volume of Pd particles through C-modified low-coordinated surface sites. Enhanced subsurface diffusion most likely allows effective replenishment of the reservoir of active subsurface H(D) species, and with this enables sustained hydrogenation. Computational results support this hypothesis and show that carbon deposition near particle edges results in a lattice expansion and a concomitant elimination of the activation barrier for hydrogen subsurface diffusion. The atomic lateral flexibility of Pd nanoparticles was identified as a crucial factor for allowing pronounced facilitation of subsurface hydrogen diffusion, an effect that is absent on the laterally rigid Pd(1 1 1) surface. Experimentally, the rate of the subsurface hydrogen diffusion was addressed by the $H_2 + D_2 \rightarrow HD$ exchange reaction in the low-temperature regime where this reaction is limited by the formation rate of subsurface H(D) species. In agreement with theoretical predictions, evidence of a pronounced enhancement of the H subsurface diffusion rate through C-modified low-coordinated sites by about an order of magnitude was observed as compared to C-free particles.

These new insights allowed us to identify an exceptionally important role of carbonaceous species in hydrogenation chemistry on nanostructured catalysts that was previously underappreciated. Small amounts of carbon adsorbed at the low-coordinated surface site of Pd nanoclusters allow effective replenishment of subsurface hydrogen under steady-state conditions, and with this enables sustained hydrogenation and is critical in controlling the overall selectivity between the two pathways. Our results also highlight the crucial role of subsurface hydrogen diffusion, which is a strongly structure-sensitive process on Pd surfaces, in the hydrogenation of the olefinic bond. These new findings challenge the universality of the common belief of the structural insensitivity of double-bond hydrogenation and demonstrate a need for developing new microscopic concepts to describe the fundamentals of hydrogenation catalysis.

Palladium is particularly important for hydrogenation catalysis due to its unique ability to stabilize hydrogen in the bulk and near subsurface region [16,34,37]. It has been long time assumed that other transition metals are not capable of producing thermodynamically stable subsurface hydrogen. However, recent NRA studies on nanosized supported Pt clusters [38] indicate that in the systems with reduced dimensionality subsurface hydrogen species can be formed also for other transition metals. This phenomenon the hydrogenation mechanism involving subsurface hydrogen might be highly relevant also for other nanosized transition metal catalysts. Further investigations are needed to verify this hypothesis.

In the present study, we hope to provide a comprehensive microscopic picture of hydrogenation processes, particularly over Pd. At the same time, the discussion above highlights some of the essential questions raised in recent years in connection with the surface chemistry of catalysis. The most important one is what is the minimal level of complexity of a model catalyst that is necessary to adequately resemble the intrinsic properties of a realistic catalytic surface? Particularly for hydrogenation catalysis, our example shows that the single-crystal model surfaces largely fail to reproduce the chemistry, which is well known in practical applications, and that the use of small atomically flexible nanoparticles is a necessary condition to achieve an atomistic-level understanding of the hydrogenation processes in steady state. It becomes evident that the structural diversity of the supported nanoparticles and the presence of surface modifiers, such as carbon and others, give rise to kinetic effects that determine the overall activity and selectivity. To study such effects, new, more realistic supported model systems need to be developed. Also a methodology capable of providing detailed kinetic information under the realistic pressure conditions combined with the spectroscopic *in situ* characterization of the active surface needs to be developed. Particularly for hydrogenation catalysis, potential formation of a hydride phase under the high-pressure reaction conditions and the consequences for the hydrogenation activity is a subject of ongoing discussion. To study this kind of effects, one would need to go beyond ultra-high-vacuum conditions to the pressure and temperature range, where the hydride phases can be formed.

In addition, the overall performance of a catalyst depends not only on the intrinsic propensity of a metal to catalyze the desired reaction pathways, but also on the ability of the catalyst to efficiently bind the reactants, stabilize the desired reaction intermediates, and effectively release the products. The latter group of properties is determined by the bond strength of the adsorbed surface species and by the relative thermodynamic stabilities of the reaction intermediates. For both aspects, the size of the active metal particles can strongly affect the adsorbates' binding strength [39] and thus crucially control activity and selectivity. A detailed knowledge of the energetics of the adsorbate–surface interaction, investigated as a function of particles' size and structure, would provide a basis for fundamental understanding of how the surface binds the reactants and guides them through various elementary steps to the products. For the practically important nanostructured materials, such fundamental information on the correlation between the gas-surface binding energy and the exact nature of an adsorption site as well as the size of the metal nanoparticles is not available at the moment and should be subject to further investigations.

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