DOI: 10.1002/cphc.201000355

Role of Low-Coordinated Surface Sites in Olefin Hydrogenation: A Molecular Beam Study on Pd Nanoparticles and Pd(111)

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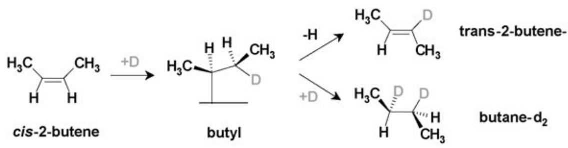
Hydrogenation of unsaturated hydrocarbon compounds catalyzed by transition metals is traditionally believed to be a structure-insensitive reaction.[1] However, recent progress in understanding the microscopic details of this process challenges the universality of this common belief. Recently, several examples of catalytic systems were described in the literature where hydrogenation of the olefinic double bond was shown to crucially depend on the presence of hydrogen species absorbed in the subsurface region of a metal catalyst.[2–4] Particularly for Pd nanoparticles, slow replenishment of these species required for hydrogenation was identified as a rate-determining process in a broad range of reaction conditions.[2–6] In view of these results, the permeability of the metal surface for hydrogen can play a crucial role in its activity in hydrogenation catalysis. Since subsurface hydrogen diffusion is known to be a strongly structure-sensitive process on Pd surfaces,[7] the degree of coordination of the surface Pd atoms can be very important in determining the formation rate of subsurface hydrogen species, and therefore may be decisive for the hydrogenation activity.

In line with this suggestion, it was recently observed experimentally that modification of the low-coordinated surface sites of Pd nanoparticles, such as edges and corners, with carbon significantly affects the hydrogenation activity and results in a sustained hydrogenation rate that is not possible on the C-free surface.[2,5] This observation was proposed to arise from faster subsurface diffusion of hydrogen through the edge sites modified with carbonaceous deposits. Recent theoretical calculations supported the hypothesis that carbon adsorbed in the vicinity of particle edges strongly reduces or nearly eliminates the activation barrier for subsurface hydrogen diffusion on Pd particles.[8] This effect was ascribed mainly to C-induced expansion of the surface openings for penetration of H into the subsurface region. In contrast, no notable reduction of the activation barrier was found with carbon on the intrinsically rigid regular Pd(111) surface.[8] The conceptual importance of atomic flexibility of sites near particles edges in subsurface hydrogen diffusion, demonstrated by the theoretical calculations, suggests that the low-coordinated surface sites can play a crucial role in the hydrogenation process.

In order to obtain more insight into the role of low-coordinated surface sites in hydrogenation, we studied the reaction of *cis*-2-butene with deuterium on well-defined model Pd nanoparticles supported on a thin Fe_3O_4/Pt(111) film. Two complementary strategies were applied herein to address the role of low-coordinated surface sites experimentally: first, we compared the hydrogenation activity of Pd particles with an extended Pd(111) single crystal surface. Secondly, we selectively modified the low-coordinated surface sites by deposition of carbon, which has previously been determined to predominantly occupy edges and corners of Pd nanoclusters,[5] and follow the reactivity changes upon such modification. Herein, we demonstrate that modification of the low-coordinated surface sites of Pd particles with carbon promotes *sustained* hydrogenation activity in a pronounced manner, while carbonaceous deposits adsorbed on the extended Pd(111) surface do not noticeably affect the reactivity. We ascribe this phenomenon to facilitation of hydrogen subsurface diffusion through carbon-modified low-coordinated sites of Pd nanoparticles, which are not available on Pd(111).

Generally, alkene conversions promoted by transition-metal catalysts are accounted for by the Horiuti–Polanyi mechanism,[9] which proceeds through a series of successive hydrogenation-dehydrogenation steps:



Particularly for *cis*-2-butene conversions with D_2, an initial half-hydrogenation transforms the adsorbed alkene into a surface 2-butyl-d_1 species, which is the common reaction intermediate for both of the possible reaction paths: *cis–trans* isomerization (accompanied by H–D exchange) and hydrogenation.[10] This butyl-d_1 intermediate can then undergo either a β-hydride elimination to form *trans*-2-butene-d_1 or a second half-hydrogenation step and incorporate a second deuterium atom to form butane-d_2. On the Pd nanoparticles, the *second* half-hydrogenation step was found to occur only in the presence of subsurface D,[2] whose replenishment was identified to be linked to the rate limiting step in a broad range of reaction conditions.[5,6]

The model catalyst used herein consists of Pd nanoparticles of ~7 nm size (Figure 1), mainly terminated by (111) facets (~80% of the surface area) and exhibit a smaller fraction of low-coordinated surface Pd atoms incorporated into edges, corners and (100) facets.[11] Carbon deposition was performed by adsorption of *cis*-2-butene and D_2 followed by heating to 485 K. The spatial distribution of the produced carbonaceous

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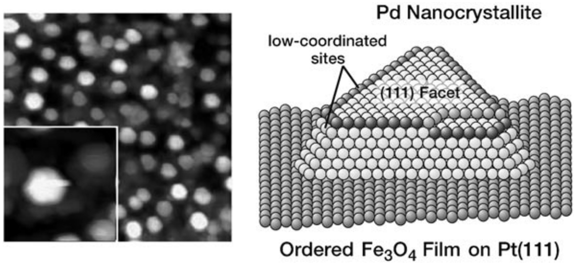

Figure 1. Scanning tunnelling microscopy (STM) image (100 nm × 100 nm, inset: 20 nm × 20 nm) of the Pd/Fe_3O_4/Pt(111) supported model catalyst used in the experiments described herein (from [11]), together with a schematic representation of the structure of the Pd nanoparticles.

deposits was previously investigated by IR spectroscopy using CO as a probe molecule for different adsorption sites. It was established that carbon occupies predominately edge sites of the Pd nanoparticles while leaving the regular (111) terraces nearly unchanged.[5]

Figure 2 shows the production rate of butane-d_2 resulting from the reaction of *cis*-2-butene with D_2 over a C-free (Figure 2a) and C-precovered (Figure 2b) Pd-supported model catalysts at 260 K, which were pre-saturated with D_2 prior to the olefin exposure. A sequence of *cis*-2-butene pulses, consisting of 50 short (4 s on, 4 s off) and 30 long (20 s on, 10 s off) ones, was applied using an independent beam source concomitant with the continuous D_2 exposure. The reaction was carried out in a large excess of D_2 with the ratio of D_2:*cis*-2-butene molecules amounting to 570. On the pristine Pd particles (Figure 2a), the initial period of high hydrogenation activity on D-saturated catalyst is followed by a decrease of the reaction rate to zero under steady-state conditions. Remarkably, carbon deposition prevents the suppression of the hydrogenation pathway in the steady state and results in persisting hydrogenation activity at the initially high level (Figure 2b). It should be noted that the reaction rate of the *cis-trans* isomerization/H–D exchange in the steady state remains very similar on both C-free and C-precovered Pd particles (not shown here, see ref. [2]), indicating that the surface concentrations of D and butyl-d_1 are not substantially affected by C deposition under the investigated conditions.

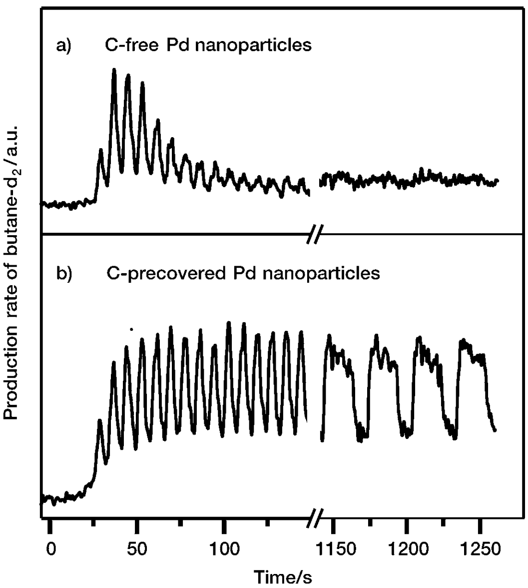

Figure 2. The hydrogenation reaction rate of *cis*-2-butene at 260 K over initially D_2-saturated a) clean and b) carbon-precovered Pd/Fe_3O_4/Pt(111) model catalysts.

The microscopic reasons for the vanishing hydrogenation activity on the C-free catalyst could be deduced recently from the combination of H-depth profiling by NRA and transient MB experiments carried out at different H_2/D_2 pressures,[2] which provided experimental evidence that the presence of subsurface H species is necessary for hydrogenation.[12] In view of this finding, the initially high hydrogenation rate (probed by the initial short pulses) on both C-free and C-precovered Pd particles can be ascribed to the high availability of *subsurface* D atoms directly after pre-saturation. However, the abundance of these species on the C-free particles cannot be maintained at the initially high level after prolonged olefin exposure, resulting in vanishing hydrogenation rates. This behavior was suggested to be a consequence of the slow D subsurface diffusion hindered by co-adsorbed hydrocarbons. In contrast, sustained hydrogenation activity of the C-precovered particles indicates effective replenishment of the subsurface D species even under steady-state reaction conditions. It is possible that hydrogen subsurface diffusion through the *C-modified edge sites* can be the reason for this observation, as was recently supported by theoretical calculations.[8]

It should be pointed out that our experimental data allow us to exclude some other possible explanations of the sustained hydrogenation on the C-modified particles. First, C-modification of the surface sites does not appear to noticeably enhance the intrinsic reactivity of the surface neither for the *cis–trans* isomerization nor for the hydrogenation pathways. This follows from very similar initial reaction rates observed on the C-free and C-precovered surfaces when no limitations in D availability are present, that is, on the D-saturated particles. Second, it appears unlikely that the sustained hydrogenation on the C-precovered particles arises from the modified binding properties of the hydrocarbon adsorbates (both butene and butyl-d_1 species) since in the opposite case the *cis–trans* isomerization pathway, which proceeds through the same hydrocarbon intermediate, has to be influenced considerably by C-deposition as well.

In order to examine the abovementioned hypothesis experimentally, the same series of pulsed MB experiments were performed at 260 K on an extended Pd(111) single-crystal surface, for comparison. Figure 3 shows the product response curves obtained for the hydrogenation pathway under steady-state conditions for Pd(111) (upper row) and Pd nanoparticles (lower row) on the C-free and C-precovered surface. On both C-free surfaces no sustained hydrogenation can be observed, pointing to limitations in availability of *subsurface* D species. It is important to note that the competing *cis–trans* isomerization/H–D exchange proceeds effectively on both C-free surfaces

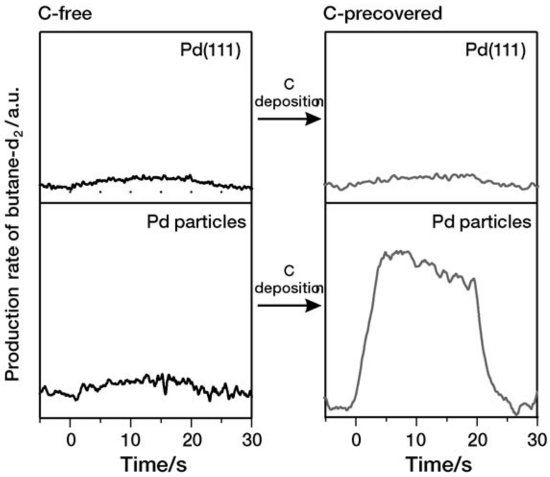

Figure 3. Averaged hydrogenation rates obtained from a series of pulsed molecular beam experiments, in which the catalyst was exposed to a continuous D_2 molecular beam and a modulated *cis*-2-butene molecular beam at 260 K. The rates were calculated by averaging the reaction rates from the last 30 long pulses of the experiment and were normalized to the number of the surface Pd atoms for quantitative comparison. Shown are the hydrogenation rates plotted as a function of time on Pd(111) (upper row) and Pd particles (lower row) on the C-free (black curves) and C-containing (grey curves) surfaces.

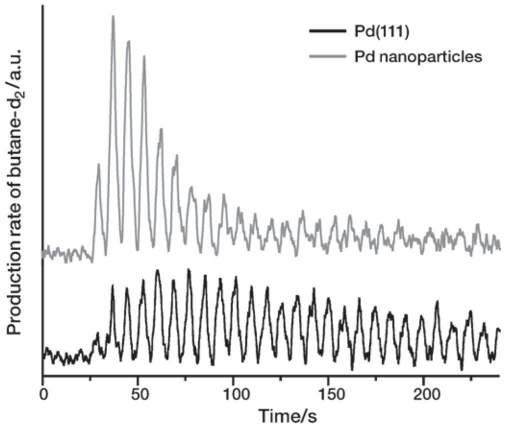

Figure 4. The initial hydrogenation rates of *cis*-2-butene obtained on C-free Pd(111) and C-free Pd particles at 260 K pre-saturated with deuterium from a series of pulsed molecular beam experiments, in which the catalyst was exposed to a continuous D_2 molecular beam and a modulated *cis*-2-butene molecular beam. The hydrogenation rates are normalized to the number of the surface Pd atoms. Background changes have been removed.

(with the reaction rates close to the initial rates on the D-saturated catalysts), indicating that there are no limitations in availability of *surface* D and adsorbed *cis*-2-butene. While on Pd nanoparticles, carbon deposition results in a sustained hydrogenation rate under steady-state conditions, this effect is not present on C-covered Pd(111), where the hydrogenation rate remains negligible. It should be emphasized that on all four catalysts [C-free and C-covered Pd(111) 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-covered Pd particles, which is higher than on C-covered Pd(111) by several orders of magnitude, cannot be ascribed to strong variations in the concentrations of *cis*-2-butene and *surface* D. This behavior strongly suggests that sustained hydrogenation on C-covered Pd nanoparticles arises from the modified properties of the low-coordinated surface sites and *not* from a C-induced modification of regular (111) terraces.

There are two conceivable ways to explain the role of low-coordinated surface sites in promotion of the long-time sustained hydrogenation activity on C-covered catalyst. First, such sites may exhibit intrinsically higher activity than the (111) facets, or secondly, they may allow for the effective replenishment of the reactive species, which are necessary for hydrogenation, on the entire particle. However, the first—seemingly simple—explanation is not supported by our experimental results. Figure 4 shows the initial hydrogenation rates obtained on the Pd nanoparticles and Pd(111) surface pre-saturated with D_2, which were normalized to the number of the surface Pd atoms for comparison (1.5×10^{15} Pd atoms cm^{-2} for Pd(111) and 0.6×10^{15} Pd atoms cm^{-2} for Pd nanoparticles). Clearly, the initial hydrogenation rates of Pd(111) and Pd particles pre-saturated with D_2 are in the same range of magnitude. This fact implies that the differences in the hydrogenation activity in the steady state, amounting to several orders of magnitude (see Figure 3 b), cannot be merely ascribed to the presence of the low-coordinated surface sites on Pd nanoparticles. Instead, this observation clearly demonstrates that Pd nanoparticles, comprising both (111) facets and low-coordinated surface sites, exhibit similar initial reactivity to Pd(111) during the time period when there are no limitations in D availability (for both surface and subsurface species).

Alternatively, the persistent high hydrogenation activity on the C-modified Pd particles can be explained by a more effective replenishment of the reactive species under steady-state reaction conditions compared to the C-free surface. Since for all four catalysts [C-covered and C-free Pd nanoparticles and Pd(111)], 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 Figure 2 b). It should be also emphasized that carbon modification of particle edges does not result in hydrogenation rates higher than on the D-saturated surface, which means that the modified surface sites are *not* inherently more active in hydrogenation. Instead, C-modification merely allows maintaining the populations of reactants, particularly *subsurface* D at a sufficiently high level.[12] 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 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 steady state hydrogenation rates similar to the initial hydrogenation rates observed on the D-saturated surface. This interpretation is in very good agreement with the recent theoretical calculations, which show a strong decrease or elimination of the activation barrier for subsurface hydrogen diffusion when carbon is adsorbed in the vicinity of Pd particle edges.[8]

In summary, we demonstrated that low-coordinated surface sites on Pd particles, such as edges and corners, play a crucial role in hydrogenation of olefins. We ascribe their role to determining how fast adsorbed hydrogen atoms diffuse into the subsurface region of Pd nanoparticles in order to build up and maintain a sufficiently high concentration of *subsurface* hydrogen species required for hydrogenation. Modification of these low-coordinated sites with carbon results in pronounced changes of the hydrogenation activity under steady-state conditions, which can be attributed to facilitated subsurface diffusion of hydrogen. This experimental result is in excellent agreement with theoretical calculations, which predict a strong reduction of the barrier for hydrogen subsurface diffusion on the C-modified edge sites of Pd nanoclusters.[8] These observations highlight the exceptional importance of modifiers, which are usually present on the catalytically active surface under reaction conditions. Related effects are expected to be general in playing a key role in controlling the hydrogenation activity for other supported transient metal catalysts as well.

Acknowledgement

We acknowledge financial support by Fonds der Chemischen Industrie and Deutsche Forschungsgemeinschaft in the very early stages of this project. The authors thank Prof. R. J. Madix and Prof. M. Wilde for valuable discussions.

Keywords: hydrogenation · nanoparticles · palladium · subsurface hydrogen · surface chemistry

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[12] It should be noted that it is not clear yet whether subsurface H(D) species participate in the reaction directly or act indirectly by changing for example, the adsorption properties of the surface H(D) species, making them more prone for attacking the metal-carbon bond of 2-butyl-d_1 intermediate.

Received: May 4, 2010