Influence of Carbon Deposition on the Hydrogen Distribution in Pd Nanoparticles and Their Reactivity in Olefin Hydrogenation**

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The accumulation of carbonaceous deposits resulting from the early decomposition of the reactants is recognized to considerably affect the activity and the selectivity in hydro-carbon conversions promoted by transition metals.[1] The underlying microscopic mechanisms of carbon-induced changes in reactivity have recently been addressed using the surface science approach for the selective hydrogenation of alkynes[2] and the isomerization and hydrogenation of alkenes.[3] In particular, we have shown that sustained activity toward hydrogenation of the olefinic double bond can be achieved only in the presence of co-adsorbed strongly dehydrogenated carbonaceous deposits.[3] However, the exact role that these carbon species play in the promotion of the persistent hydrogenation activity remained unknown.

Generally, promotion of olefin hydrogenation appears to be closely connected to the adsorption state of hydrogen atoms on the metal catalyst. The traditional opinion that only surface hydrogen species are involved in the hydrogenation process[1] was questioned for the first time by Ceyer et al.[4] More recent studies on supported nanoparticles[5,6] revealed the crucial role of weakly bound volume-absorbed hydrogen species in alkene hydrogenation. Specifically, high hydro-genation activity under low-pressure conditions was observed on Pd clusters but not on single crystals; this was attributed to the unique ability of the small particles to store large amounts of hydrogen atoms in a confined volume. Still, the involve-ment of the volume-absorbed hydrogen atoms in the olefin hydrogenation remained a controversial issue, mainly because of the experimental difficulty in detecting the hydrogen species present under the isothermal reaction conditions.

Recently, we overcame this limitation by applying ^{1}H-$(^{15}$N,$\alpha\gamma)^{12}$C nuclear reaction analysis (NRA) for hydrogen depth profiling to separately monitor the surface-adsorbed and volume-absorbed hydrogen species in Pd nanoparticles supported on a model oxide film. We reported the first direct observation of substantial hydrogen absorption in the volume of metal clusters under low pressure conditions.[7] In the present study, we combine NRA hydrogen depth profiling of Pd nanoparticles with transient molecular beam reactivity measurements to answer two closely related questions: 1) What is the role of the different hydrogen species in the hydrogenation of the olefinic double bond, and 2) how do the carbonaceous deposits affect the hydrogen distribution in the Pd nanoparticles to promote the sustained catalytic activity?

As a result, we obtained the first direct experimental evidence that the presence of H absorbed in the Pd particle volume is required for olefin hydrogenation. We further show that even a submonolayer coverage of carbon significantly affects the H depth distribution in the Pd particles. We attribute the sustained hydrogenation activity, promoted by carbonaceous deposits, to the facilitation of H diffusion into the particle volume under the reaction conditions, which results in the enhanced ability of the Pd clusters to replenish the volume-absorbed H atoms required for hydrogenation.

Our experimental approach is illustrated in Figure 1. We employed well-defined Pd model catalysts prepared in situ under ultra-high-vacuum conditions on model thin oxide films.[8] The catalytic activity of the Pd clusters in the reaction of *cis*-2-butene with D_2 was probed by molecular beams (MB) under isothermal conditions (Figure 1a). Under identical conditions, complementary high-resolution hydrogen depth profiling by grazing ion incidence NRA was performed, which distinguishes surface-adsorbed H from H absorbed inside the Pd clusters (Figure 1b).[7] Two types of model catalysts were used in this study: Pd particles supported on a Fe_3O_4/Pt(111) film for the reactivity measurements and Pd clusters grown on an Al_2O_3/NiAl(110) model support for hydrogen depth profiling. The microscopic structure and morphology of both catalysts were investigated in detail previously.[8–10] In both cases, the three-dimensional Pd particles have a well-defined crystalline structure and similar average diameters (roughly 6 nm for the Pd/Al_2O_3/NiAl(110) and 7 nm for the Pd/Fe_3O_4/Pt(111) catalysts; Figure 1c). It is important to emphasize that the properties toward dissociative H_2 adsorp-

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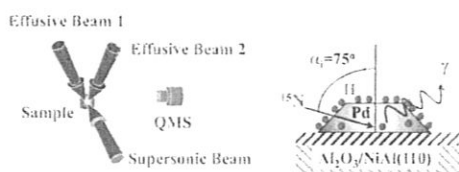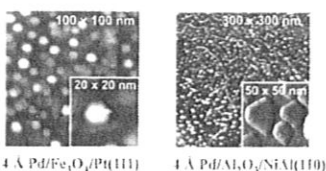
c) Supported Model Catalysts

Figure 1. a) Setup for the UHV molecular beam experiment for the reaction kinetics measurements; b) setup for the grazing incidence NRA experiment for H depth profiling in the Pd nanoclusters; c) scanning tunneling microscopy images of the Pd/Fe₃O₄ and Pd/Al₂O₃ catalysts.

tion and the reactivity behavior of both catalysts are dominated by the Pd nanoclusters and not by the supports. Both oxides were proved to be inactive in H_2 dissociation to produce atomic H, and hence they are completely inert in the alkene conversions. In addition, the nature of the support was found not to affect the properties of the supported Pd clusters towards dissociative H_2 ad-/absorption; this was evidenced by temperature-programmed desorption spectra, which exhibit nearly identical peak positions and intensity ratios for the surface and the subsurface/bulk adsorption states. These observations confidently justify the use of the Pd/Al₂O₃ catalyst for H profiling measurements as an appropriate proxy for the Pd/Fe₃O₄ model system applied in the reactivity measurements (see the Supporting Information for more details).

Alkene conversions with H_2 are generally described by the Horiuti–Polanyi mechanism,[11] which proceeds through a series of successive hydrogenation–dehydrogenation steps as shown in Scheme 1 for *cis*-2-butene. In this case an initial half-deuteration forms a surface butyl species, which is a common
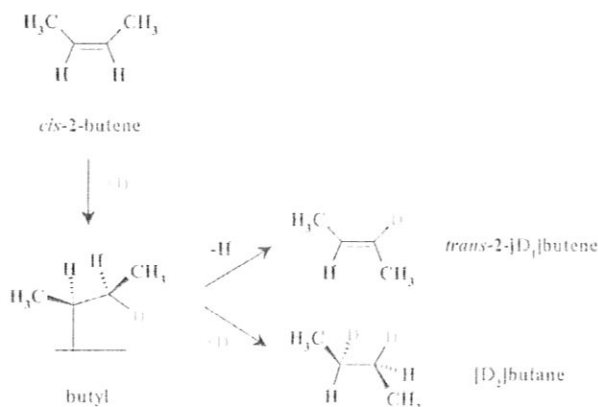
Scheme 1.

reaction intermediate for both possible *cis–trans* isomerization (accompanied by H–D exchange) and hydrogenation reactions.[1,12] The butyl intermediate can either undergo a β-hydride elimination to form *trans*-2-[D₁]butene or incorporate a second deuterium atom to form [D₂]butane. Dehydrogenation of the adsorbed alkene to give other carbonaceous surface species is also possible.[1,12]

Figure 2 displays the results of reaction rate measurements for hydrogenation and *cis–trans* isomerization of *cis*-2-butene on the initially clean and carbon-precovered Pd

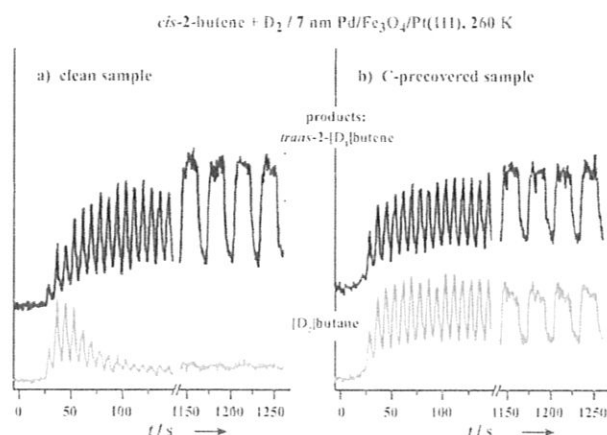*cis*-2-butene + D₂ / 7 nm Pd/Fe₃O₄/Pt(111), 260 K

Figure 2. Time evolution of the main reaction products in isomerization (*trans*-2-[D₁]butene) and hydrogenation ([D₂]butane) of *cis*-2-butene at 260 K over initially D₂-saturated clean (a) and carbon-precovered (b) Pd/Fe₃O₄/Pt(111) model catalysts.

particles. The catalyst was first pre-exposed to a continuous D_2 beam to saturate the particles; after that, a sequence of *cis*-2-butene pulses was applied using an independent beam source while D_2 exposure was continued. On the initially clean particles (Figure 2a), both reaction pathways exhibit a short induction period[3] followed by a period of high activity. However, only *cis–trans* isomerization is sustained over extended periods of time, whereas the hydrogenation rate quickly decreases and approaches zero. Remarkably, not only isomerization but also hydrogenation is maintained under steady-state conditions on the catalyst that was precovered with carbon prior to the reaction (Figure 2b). This unique catalytic behavior clearly demonstrates the promoting role of carbon in the persistent hydrogenation activity of the Pd catalyst.

Two major closely related questions arise from these observations: 1) Why is the hydrogenation pathway selectively suppressed under the steady-state reaction conditions on the initially clean particles, and 2) what is the role of carbon in the induction of the sustained hydrogenation activity?

The sustained isomerization activity on the initially clean Pd particles implies that both the butyl intermediate and adsorbed D atoms are available under the steady-state conditions. Therefore the selectively vanishing hydrogenation activity strongly suggests that this pathway cannot solely be dependent on the apparently abundant surface D. It appears

that the second half-hydrogenation of butyl to butane requires the presence of a certain type of D atoms, which are populated in the Pd particles saturated with D at the beginning of the reaction but cannot be replenished under the steady-state conditions.

To investigate the exact nature of these particular D/H species, we determined the abundance of surface-adsorbed and volume-absorbed H atoms at different H_2 pressures by NRA and studied in parallel the transient kinetics of both reaction pathways upon D_2 pressure variations in MB experiments. Figure 3a shows NRA yield curves for the alumina-supported Pd clusters exposed to H_2 at 94 K in the pressure range of $(1 \times 10^{-7}–2 \times 10^{-5})$ mbar. Each curve, which contains the H depth distribution, can be deconvoluted into two components, corresponding to the surface-adsorbed H[7,13–15] and the volume-absorbed H (Figure 3b).[16] The coverage of surface H saturates first at a H_2 pressure below 1×10^{-6} mbar while the concentration of cluster-absorbed H remains strongly pressure dependent up to at least 2×10^{-5} mbar. The much earlier saturation of the surface H coverage results from the higher adsorption energy of H atoms on Pd surfaces (≈ 0.5 eV per H atom[17]) compared to the enthalpy of H

absorption in the clusters (≈ 0.28 eV at H/Pd < 0.2 and ≈ 0.1 eV per H atom at H/Pd > 0.5[7]) and implies that the cluster-absorbed H state is considerably more weakly bound than the surface-adsorbed species. Note that the quantities of volume-absorbed H are quite substantial compared to the surface H saturation coverage and even small H_2 pressure variations change the amount of volume-absorbed H species by numbers comparable with the number of the surface-adsorbed H atoms.

The corresponding reactivity measurements on the carbon-precovered Pd/Fe$_3$O$_4$/Pt(111) catalyst are displayed in Figure 4. The model catalyst was pre-exposed to D_2 and cis-
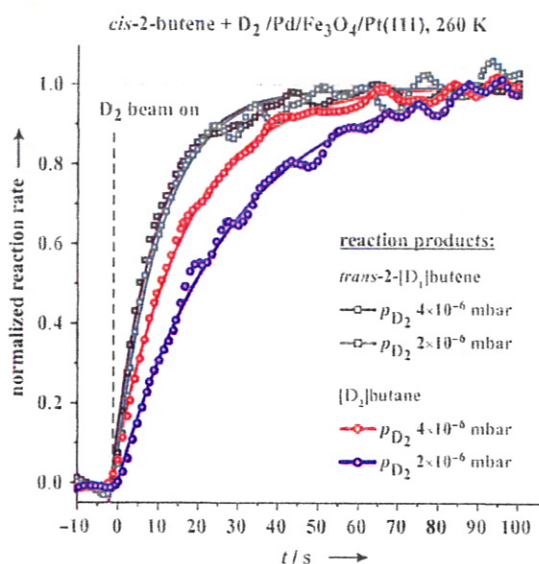
Figure 4. Time evolution of the normalized reaction rates for the isomerization (to give trans-2-[D$_1$]butene) and hydrogenation (to give [D$_2$]butane) in the reaction cis-2-butene + D_2 after a temporary intermission of the D_2 beam. The reaction rates are obtained at 260 K over the C-precovered Pd/Fe$_3$O$_4$/Pt(111) catalyst at different D_2 pressures (2×10^{-6} mbar and 4×10^{-6} mbar) with the constant cis-2-butene/D_2 ratio.
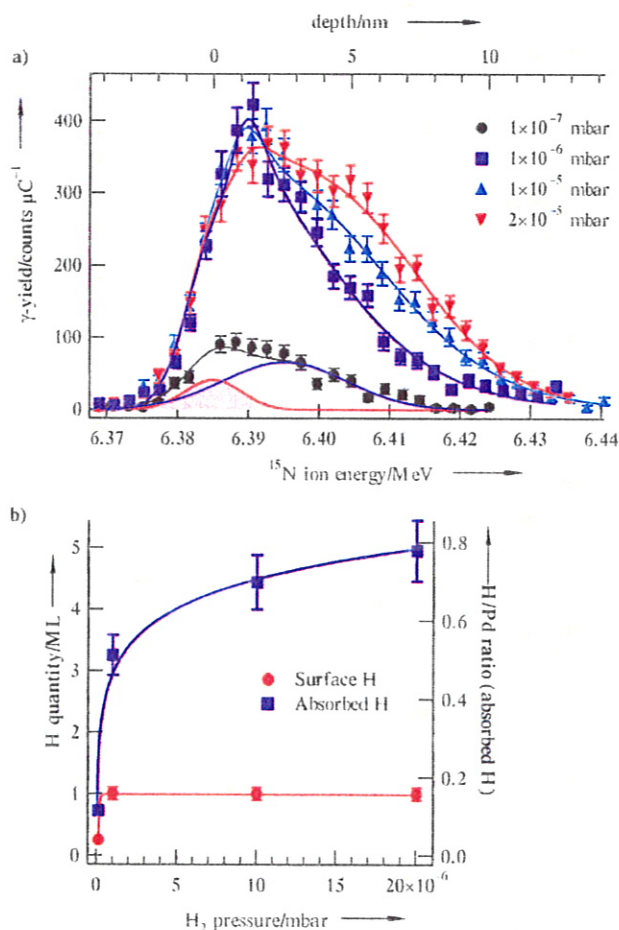

Figure 3. a) Grazing incidence NRA yield curves of H in Al$_2$O$_3$-supported Pd nanoclusters under various H_2 pressures at 94 K. b) H_2-pressure dependence of surface-adsorbed and cluster-absorbed H.

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-[D$_1$]butene) and hydrogenation ([D$_2$]butane) products was monitored as a function of time. This experiment was carried out at 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 levels as in the steady-state regime before termination of the D_2 beam. However, the transient time evolution of the reaction products in the two pathways exhibits very different behavior and D_2 pressure dependence. At both D_2 pressures the isomerization rate returns to the steady-state level with a short and very similar characteristic time constant, that is, $\tau_{char} = (11.0 \pm 0.3)$ s and (11.4 ± 0.3) s, respectively. In contrast, the evolution of the hydrogenation rate is substantially slower and exhibits a pronounced pressure dependence with characteristic times of

(18.3 ± 0.3) s and (28.3 ± 0.5) s at 4×10^{-6} mbar D_2 and 2×10^{-6} mbar D_2, respectively. It should be emphasized that the time evolution of both reaction products reflects the formation rate of atomic D species on and in the Pd clusters, which accumulate only slowly on the surface covered with an excess of hydrocarbons because of hindered D_2 dissociation.

The fast and pressure-independent time evolution of the isomerization product suggests that this pathway is linked to the coverage of surface D atoms, which are expected to build up first when the D_2 beam is resumed owing to the large heat of adsorption and to saturate at much lower pressures than the volume-absorbed D. 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 (Figure 3), this observation strongly suggests that volume-absorbed H(D) species are required for the second step in the hydrogenation reaction. It is also important to note that the D species required for hydrogenation cannot be the surface-adsorbed D, as in this case the time evolution of [D_2]butane should be pressure-independent just as the time evolution of the isomerization product *trans*-2-butene. The substantially slower recovery of the hydrogenation rate relative to the isomerization rate is a natural consequence of the fact that D atoms have to diffuse from the surface into the cluster volume, which is an activated process, whereas D_2 dissociation on Pd occurs spontaneously.[18]

Having established the nature of the H(D) atoms involved in the hydrogenation, we can now explain the observations displayed in Figure 2. On the initially clean particles presaturated with D_2 prior to olefin exposure, both surface and bulk hydrogen states are populated, which results in the high initial rates of both reaction pathways. After the prolonged olefin exposure, hydrogenation becomes selectively suppressed because the bulk D species are consumed and cannot be replenished under the steady-state reaction conditions. This inability to populate the volume-absorbed D arises from the fact that during olefin exposure the surface D atoms can either diffuse into the particle volume or be consumed in the reaction with hydrocarbons. Apparently, the D diffusion into the bulk becomes negligible as a consequence of the competition with the isomerization reaction and therefore the hydrogenation rate decreases to zero.

It is important to emphasize that the crucial role of the volume-absorbed H species for the hydrogenation route does not necessarily mean that these species are directly involved in the second half-hydrogenation step. Alternatively, the presence of volume-absorbed H might merely modify the adsorption and/or the electronic properties of surface H, making it more prone to react with alkyl species to form alkane. Further theoretical work is needed to understand the underlying microscopic mechanism of this process.

The sustained hydrogenation activity observed on the C-precovered catalyst suggests that this surface is capable of replenishing the volume-absorbed D under the steady-state conditions even in competition with the isomerization reaction. This means that the co-adsorbed carbonaceous species most likely facilitate the D diffusion from the surface into the particle volume.

Further experimental insights corroborating this conclusion were provided by the H depth distributions obtained on the clean and C-precovered Pd particles (Figure 5). With each deposition cycle, which produces submonolayer amounts of carbonaceous species on the surface,[3] the amount of
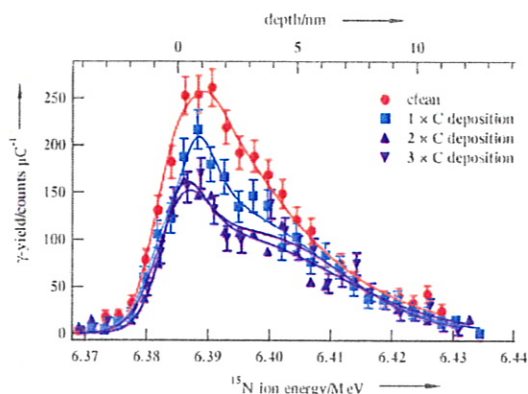

Figure 5. NRA yield curves representing the change of the H distribution in the Pd/Al$_2$O$_3$/NiAl(110) model catalyst under the conditions of *cis*-2-butene conversion (260 K, 4×10^{-6} mbar H$_2$) induced by successive carbon depositions. Each carbon deposition cycle was performed according to the procedure described in the Supporting Information.

H species on and closely below the surface is reduced, whereas the amount of H absorbed deep in the cluster volume remains unaffected. However, H-profiling measurements carried out at 94 K (data not shown) reveal that the saturation coverage of surface H and the amount of deeper bulk H are identical on the clean and C-covered particles and that only the H abundance closely below the surface is reduced by C; this is in good agreement with recent theoretical calculations on Pd clusters predicting C diffusion into the subsurface region.[19] This means that submonolayer amounts of C do not sterically block the surface of Pd particles for hydrogen adsorption but only energetically destabilize surface H by weakening the metal–hydrogen bond. As a result the stationary H coverage on the C-precovered surface under the reaction conditions (260 K) is slightly reduced compared to the clean particles. Additionally, the fact that C deposition does not increase the amount of volume-absorbed D atoms strongly suggests that the promotion of sustained hydrogenation activity on the C-pretreated surfaces does not result from the accumulation of larger amounts of D atoms in the particle volume but arises most likely from the enhanced rate of D diffusion into the bulk. There are two conceivable ways in which co-adsorbed carbon might facilitate the H(D) diffusion into the bulk. First, the lowering of the adsorption energy of the surface H species by co-adsorbed C will lead to a noticeable reduction of the activation barrier for the surface to bulk diffusion.[18] Alternatively, C species incorporated into the Pd particles might cause Pd lattice distortions, so that the surface becomes more permeable for H(D).

In summary, we have proven experimentally that hydrogenation of the olefinic double bond requires the presence of

weakly bound H species absorbed in the Pd particle volume. Carbon deposition strongly affects the H depth distribution in the Pd particles and promotes persistent hydrogenation activity. We attribute the promotion of the sustained hydrogenation by the carbonaceous deposits to the facilitation of hydrogen diffusion from the surface into the bulk of the Pd particles, allowing a fast replenishing of the volume-absorbed hydrogen atoms.

These observations highlight the exceptional importance of modifiers which are usually present on catalytically active surfaces under reaction conditions. Related effects are expected to play a key role in controlling selectivity in all types of hydrocarbon reactions on supported noble-metal catalysts.

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