

# Hydrogenation on Metal Surfaces: Why are Nanoparticles More Active than Single Crystals?\*

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Hydrogenation of unsaturated hydrocarbons occurs efficiently on noble-metal catalysts, such as platinum, rhodium, and palladium.<sup>[1]</sup> The reaction mechanism first proposed by Horiuti and Polanyi<sup>[2]</sup> in 1934 proceeds by a) hydrogen dissociation on the metal surface, b) alkene adsorption, c) subsequent hydrogen addition to alkene and, finally, d) desorption of the product (alkane). Real hydrogenation catalysts represent very complex systems for studying reaction mechanisms at the molecular level. Therefore, model systems with a reduced complexity have been invoked ranging from single crystals to metal particles deposited on oxide films.<sup>[3–8]</sup> The conclusions regarding reaction mechanism and structural sensitivity are often based upon experiments on single metal crystals.<sup>[3]</sup> In particular, hydrogenation of alkenes has been shown to be structure insensitive.

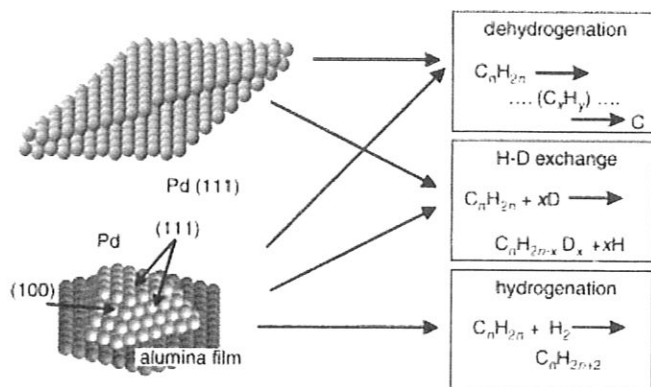
Herein, we report results showing that alkene hydrogenation reaction under low-pressure conditions, which does not occur on Pd(111) single crystal, proceeds efficiently on palladium nanoparticles. We show that the formation of weakly bound “subsurface” hydrogen is a key factor for hydrogenation to occur efficiently. The subsurface hydrogen exists in both Pd systems. However, the nanoparticle dimensions are such that this hydrogen is accessible to the adsorbed alkene, and hydrogenation occurs. In contrast, for crystals, the hydrogen atoms diffuse so deep into the bulk that they are not accessible to an adsorbed alkene, and therefore hydrogenation does not occur.

We have studied the surface chemistry of ethene and different pentene isomers on both Pd(111) single crystal and Pd particles deposited on a thin alumina film (Figure 1). The particles studied are approximately 5 nm in diameter and consist primarily ( $\approx 90\%$ ) of (111) facets<sup>[8]</sup> ( $\approx 10\%$  are (100) facets). The experiments were performed in ultrahigh vacuum on clean and well-defined systems. Using the temperature-programmed desorption (TPD) technique, we have observed that a number of hydrocarbon transformations, such as dehydrogenation and H–D exchange, occur on both palla-

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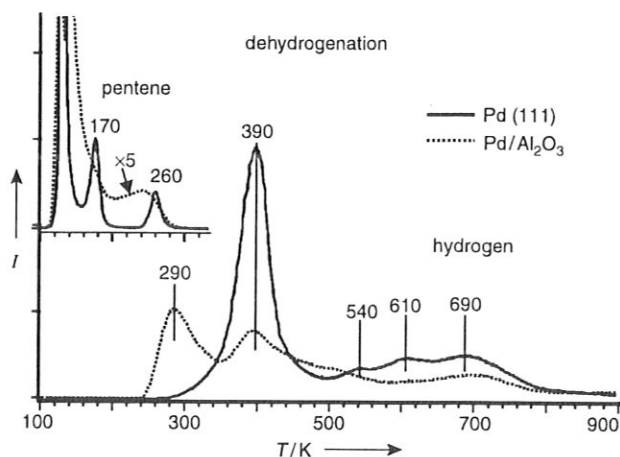
**Figure 1.** Schematic representation of the alkene reactions observed on Pd(111) single crystal (top) and well faceted Pd nanoparticles supported on a thin alumina film (bottom).

dium systems. However, the hydrogenation to alkane only occurs on small particles.

Adsorption of light alkenes, such as ethene, on palladium has been the subject of extensive studies on single-crystal surfaces and supported catalysts.<sup>[9,10]</sup> There is considerably less data on the interaction of higher hydrocarbons.<sup>[11–14]</sup> Madix and co-workers studied the adsorption of various alkenes and dienes on the clean and hydrogen (deuterium) precovered Pd(111) and Pd(100) surfaces by TPD.<sup>[11,12]</sup> They observed an H–D exchange reaction, which was assumed to proceed via a half-hydrogenated intermediate species. However, formation of the alkane was not observed on both surfaces.

We have examined the reactions of ethene, 1-pentene, *trans*- and *cis*-2-pentene on Pd(111) single crystals and supported Pd particles.<sup>[15–17]</sup> Herein, we only report the main results for *trans*-2-pentene, which is referred to as “pentene” in the following, while the details will be presented in a forthcoming paper.<sup>[17]</sup>

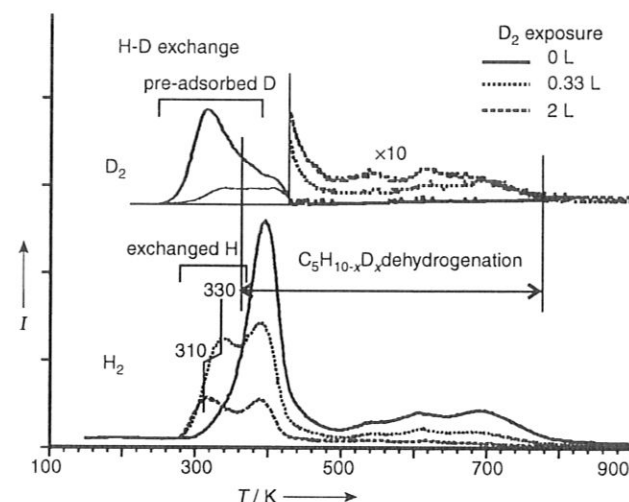
The TPD spectra for pentene on both Pd(111) and the supported Pd nanoparticles show that the molecules desorb intact at temperatures below 280 K (Figure 2). In analogy to



**Figure 2.** TPD spectra for 1 L of pentene adsorbed at 100 K on Pd surfaces

other alkene molecules previously studied,<sup>[9–12]</sup> we have assigned the desorption peaks at about 130 K to a condensed layer, at around 170 K to  $\pi$ -bonded and at approximately 260 K to  $\sigma$ -bonded pentene molecules. Upon further heating, the chemisorbed molecules dehydrogenate in a stepwise manner, as shown by hydrogen evolution extending to 800 K (cf. up to 500 K for ethene). However, the desorption of hydrogen formed on the Pd particles starts at around 100 K lower than Pd(111), although pentene desorbs molecularly at nearly the same temperatures for both systems. A similar effect is found for ethene: hydrogen starts to desorb at about 300 K from the Pd particles and at around 350 K from Pd(111). Therefore, one can conclude that alkene dehydrogenation on the particles occurs more readily than on Pd(111) crystal.

When pentene molecules are exposed to a D<sub>2</sub>-precovered Pd(111) surface, a new hydrogen peak at 330 K emerges while desorption at  $T > 390$  K is decreased (Figure 3). This result



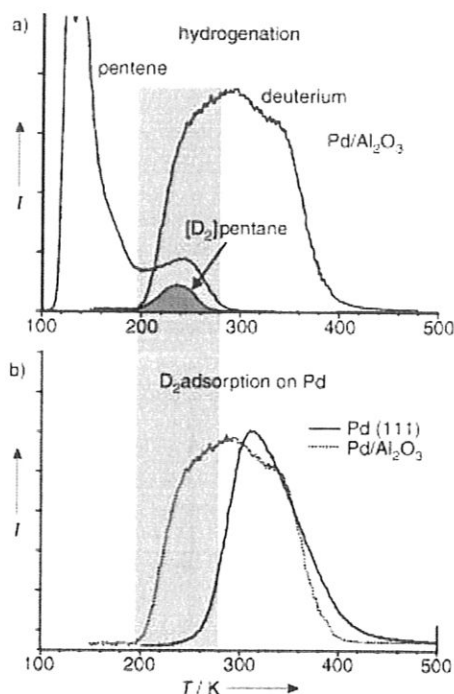
**Figure 3.** H<sub>2</sub> and D<sub>2</sub> TPD traces after pentene adsorption on the Pd(111) surface pre-exposed to different amounts of D<sub>2</sub>. D<sub>2</sub> was first adsorbed at 200 K and then 1 L of C<sub>5</sub>H<sub>10</sub> was added at 100 K.

can be understood in terms of an H–D exchange between pre-adsorbed D atoms and a half-hydrogenated alkene on the Pd(111) surfaces.<sup>[12]</sup> As a result, H atoms and D-hydrogenated pentyl species, such as C<sub>5</sub>H<sub>9</sub>D and C<sub>5</sub>H<sub>8</sub>D<sub>2</sub>, are formed. The deuterated pentenes desorb at approximately 260 K, identically to unlabeled pentene and dehydrogenate upon heating, which leads to D<sub>2</sub> evolution at 400–800 K. The H atoms, released from pentene and exchanged with D on the surface, recombine and desorb as H<sub>2</sub> and HD at 310–330 K (Figure 3).

As the D<sub>2</sub> exposure increases, the formation and subsequent dehydrogenation of C<sub>5</sub>H<sub>10-x</sub>D<sub>x</sub> species is gradually suppressed as the quantity of H<sub>2</sub> desorbing above 400 K decreases. However, the extent of the H–D exchange reaction increases with increasing D<sub>2</sub> exposure. Therefore, the amount of D<sub>2</sub> produced by dehydrogenation of surface C<sub>5</sub>H<sub>10-x</sub>D<sub>x</sub> species above 400 K increases with increasing D<sub>2</sub> coverage (Figure 3).

Meanwhile, the molecular desorption of  $C_5H_{10}$  at 170 K, previously assigned to  $\pi$ -bonded pentene, increases on the D-precovered surface (not shown here). This situation means that pre-adsorbed  $D_2$  favors pentene desorption from the  $\pi$ -bonding state, but inhibits both formation of  $\sigma$ -bonded pentene and the dehydrogenation reaction. However, pentane the product of pentene hydrogenation (and ethane, for the case of ethene) has not been detected for the co-adsorption experiments on Pd(111) surfaces.

On Pd particles pre-exposed to  $D_2$ , the results are quite similar to those obtained on Pd(111) as far as the H-D exchange reaction is concerned. However, in contrast to the Pd(111) crystal, we have observed deuterated pentane  $C_5H_{10}D_2$  (Figure 4a; and  $C_2H_4D_2$  with ethene<sup>[15]</sup>) as a product of the hydrogenation reactions. Therefore, our data clearly demonstrate that alkene hydrogenation to alkane is observed on the Pd nanoparticles only and not on the Pd(111) (and Pd(100)<sup>[11]</sup>) single crystals.



**Figure 4.** a) TPD spectra of molecular desorption of  $C_5H_{10}$  and  $D_2$  after individual adsorption, and the desorption of  $C_5H_{10}D_2$  in co-adsorption experiments on the palladium nanoparticles. b) Comparison of  $D_2$  TPD spectra for two palladium systems (1.3 L  $D_2$  at 200 K in each case).

Clearly, when dealing with the effects of small particles the presence of low-coordinate atoms, such as edge and corner atoms has to be considered. However, we have inspected a Pd(111) surface that was the roughened but again found no hydrogenation activity. Therefore, we conclude that surface roughness alone is not sufficient to provide the active sites necessary for the hydrogenation reaction to occur.

The lack of alkene hydrogenation on palladium single crystals has been discussed<sup>[12]</sup> in comparison to the results on

platinum surfaces which show hydrogenation activity for various alkenes.<sup>[18–20]</sup> It was suggested that the strength of the metal–hydrogen bond could be responsible for such a difference, because a distinctly different mechanism is unlikely.<sup>[12]</sup> Therefore, to understand why palladium particles are active for hydrogenation, we have examined the interaction of hydrogen with the palladium systems studied.

It is well documented that  $H_2$  readily dissociates on palladium, and that hydrogen atoms then migrate into the subsurface region and into the bulk, occupying interstitial sites.<sup>[21–24]</sup> When Pd is exposed to  $H_2$  above 200 K, the H atoms can diffuse so deep into the bulk that they cannot be totally released during a TPD run. However, for the nanoparticles the diffusion length is limited by the particle size, and therefore both subsurface and surface hydrogen can be detected by TPD.

Figure 4b shows  $D_2$  TPD spectra for Pd(111) and Pd nanoparticles. The broad signal observed for the particles can be deconvoluted into three peaks centered at around 340, 280, and 240 K.<sup>[15]</sup> We have previously assigned the high-temperature state to surface hydrogen (deuterium), while the low-temperature states below 300 K correspond to the presence of subsurface hydrogen.<sup>[15]</sup> Only one peak is observed for Pd(111), although surface and subsurface sites are occupied by hydrogen at these exposures.<sup>[24]</sup> This is probably due to the small energy difference between the two states.<sup>[25]</sup>

Therefore, Figure 4b clearly shows that the palladium nanoparticles contain a significant fraction of hydrogen which is more weakly bound than in Pd(111) single crystals. On the other hand, molecular pentene desorption is quite similar for both Pd systems (see Figure 2). Therefore, it is the difference in the hydrogen adsorption behavior that results in different pentene hydrogenation activity of Pd(111) crystals and Pd nanoparticles. Basically the same results are observed for experiments with ethene on Pd particles.<sup>[15]</sup> Therefore, we conclude that weakly bonded subsurface hydrogen is a key species for the occurrence of alkene hydrogenation.

Figure 4a, shows the TPD traces of molecular desorption of pentene and  $D_2$ , observed for individual adsorption, and of  $[D_2]$ pentane observed in the co-adsorption experiments. It is clear that pentane is formed and desorbs from the Pd particles over a temperature range where the  $C_5H_{10}$  and  $D_2$  desorption curves overlap. This overlap is not found for the Pd(111) crystal and as a result the hydrogenation reaction does not occur.

Figure 4b also shows that the active hydrogen state overlaps with that of  $\sigma$ -bonded pentene. As the latter state is involved in the H-D exchange reaction via half-hydrogenated pentyl species, it seems likely that hydrogenation proceeds by further addition of hydrogen to the pentyl group and subsequent desorption.

In contrast, for the reactions of ethene, we have observed that hydrogen TPD states must overlap with states assigned to the  $\pi$ -bonded ethene for the hydrogenation reaction to proceed efficiently.<sup>[15]</sup> This situation agrees well with the notion that  $\pi$ -bonded ethene is the reactive species in the ethene hydrogenation reaction.<sup>[9,10]</sup> Therefore, the overlapping of TPD states can be used to deduce which adsorbed alkene species is actually active for hydrogenation.

In conclusion, we have studied and compared the surface chemistry of ethene and *trans*-2-pentene on Pd(111) single crystal and Pd nanoparticles by TPD. We have observed that dehydrogenation and H–D exchange reactions occur on both Pd systems. However, the alkene hydrogenation to alkane has been observed only on the nanoparticles. We have shown that formation of weakly bonded subsurface hydrogen is the key factor for the hydrogenation reaction to occur. The accessibility of these hydrogen atoms is enhanced on the particles as a result of their nanoscale dimensions. This explains why nanoparticles are more active than single crystals for alkene hydrogenation under vacuum conditions. However, under real reaction conditions, it is likely that hydrogenation may also occur on Pd crystals, owing to the enhanced accessibility of subsurface hydrogen formed at high pressure.

### Experimental Section

The experiments were performed in an UHV chamber (the base pressure below  $10^{-10}$  mbar) equipped with low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), and a differentially pumped quadrupole mass spectrometer. A Pd(111) single crystal (Goodfellow) was spot-welded to two parallel Ta-wires for resistive heating. The temperature was measured by a thermocouple spot-welded to the backside of the crystal. The cleanliness of the Pd(111) crystal was first checked by AES, and then by oxygen adsorption at 300 K and monitoring CO and CO<sub>2</sub> TPD traces while subsequently heating.

The thin alumina film was prepared by oxidation of a clean NiAl(110) crystal surface as described in ref.[8]. No alkene dehydrogenation was observed on the alumina film.

Palladium (99.99%, Goodfellow) was deposited onto the alumina film at 300 K using a commercial evaporator (Focus EFM3). The morphology of the Pd particles on the Al<sub>2</sub>O<sub>3</sub>/NiAl(110) film has already been studied extensively by STM and other methods.<sup>[8]</sup>

The gas exposure, measured in Langmuir (1 L =  $10^{-6}$  mbars), was performed with a directional gas doser. D<sub>2</sub> (99.9%, isotopic content 99.5%) was supplied by AGA Gas. *trans*-2-pentene (99%, Fluka) was carefully purified by freeze-thaw cycles prior to adsorption. TPD runs were performed with a heating rate of 5 Ks<sup>-1</sup>.

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